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# FIRST PRINCIPLES OF CHEMISTRY.

---

S. COOKE.



## WORKS BY PROF. COOKE.

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FIRST PRINCIPLES OF ASTRONOMY, for Schools and Colleges. *Fifth edition, revised*, 1/6.

FIRST PRINCIPLES OF CHEMISTRY. An Introduction to Modern Chemistry for Schools and Colleges. *Sixth edition, revised*, crown 8vo, 2/6.

THE STUDENT'S PRACTICAL CHEMISTRY. Test Tables for Qualitative Analysis. *Third edition, revised and enlarged*, demy 8vo, 1/-.

FORESTS AND RAB IN INDIA. Being letters to the *Bombay Gazette*, reprinted for Students attending Forest and Agricultural Classes, price 2d.

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G. BELL & SONS, LONDON & BOMBAY.

FIRST

# PRINCIPLES OF CHEMISTRY

AN INTRODUCTION TO MODERN CHEMISTRY  
FOR SCHOOLS AND COLLEGES.

BY  
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*SIXTH EDITION—REVISED.*

LONDON :  
GEORGE BELL & SONS;  
AND BOMBAY.

1895.

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*'The beginning of Chemistry is pleasure ; its progress, knowledge ;  
its objects, truth and utility.'* ---DAVY.

## P R E F A C E

THIS little book contains (in a condensed form) the *introductory portion* of the annual course of Chemical Lectures delivered to the students of the College of Science, Poona.

It would seem scarcely necessary to remark that the present volume is by no means to be regarded as a Treatise on Chemistry ; but, on the contrary, it is intended (as the title page indicates) to serve as an introduction to the already numerous and, I may say, encyclopædic treatises on the subject by modern authors. With this object in view, I have endeavoured to develop the *leading principles* of the science in a simple but connected and logical order, suited, alike, to the wants of the student preparing for his examination, as to those of the general reader, who, in these days of scientific progress, cannot afford to be completely ignorant of the fundamental principles of Chemistry.

I have undertaken the work with the view of providing, for the students attending my own lectures, an Introductory Text-Book, which should, at the same time, be sufficiently elementary to meet the moderate requirements of *all students* preparing for University Matriculation,

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## CHAPTER I.

### METRIC SYSTEM.

The first lesson a boy has to learn, when he determines to study Chemistry, is the decimal system of weights and measures, known as the *Metric System*.

I am quite sure you will admit that the most difficult book you ever had to learn was the *Penny Table Book* of British Weights and Measures, containing probably some 20 pages or more of the most confused and unscientific stuff imaginable. A French boy can write all his tables on the palm of his hand, and so can you when you have learnt the Metric System.

This system was established in France in the year 1798, and after the lapse of nearly 100 years England's eyes have seen that it is more scientific and advantageous than its own. By Act of British Parliament (27 and 28 Vict., cap. 117, 29th July, 1864) the use of the Metric System of Weights and Measures has been rendered legal. The weight of the Kilogramme (as laid down by that Act) is 15432·3487 English grains.

The base of the system is the *metre*—from the Greek μέτρον (metron) a measure—which is a standard rod of platinum made by Borda to represent, at 0° C., the one-ten millionth part of a quadrant of the meridian of Paris. Copies of this rod, then, denote metres at the temperature 0° C.

The metre is the *unit of length*, and is sub-divided and multiplied in accordance with the decimal scale; the *tenth*, *hundredth* and *thousandth* parts are called *decimetre*,

*centimetre* and *millimetre* respectively. The multiples by 10, 100, 1,000 and 10,000 are called *decametre*, *hectometre*, *kilometre* and *myriametre* respectively.

The *unit of superficial, or square*, measure is a square, each side of which is *one decimetre* in length, and is called an *are*—from *area*, an open space. The *are* is subdivided and multiplied in the same manner as the metre.

The *unit of capacity, or of cubic* measure, is a cube, each edge of which is *one decimetre* in length, and is called a *litre*—from *litra*, a liquid measure. The *litre* is divided and multiplied according to the decimal scale.

*Note.*—For measuring timber, &c., the *cubic metre* is generally used, and is called a *stere*—from *στερεος* (stereos) solid.

The *unit of weight* is the weight of *one cubic centimetre* of distilled water at its maximum density (*i.e.*, at the temperature 4° C.), and is called a *gramme*—from *γραμμά* (gramma), figuratively used for a small weight. It, like the metre, litre, &c., is subdivided and multiplied decimally.

As we are about to adopt these measures universally, it will be well, in order to avoid mispronunciation, &c., to remove their French aspect and Anglify the names of the *units* by spelling them thus—

*meter, are, liter, gram.*

These being the units we may write our table-book as follows—reading both ways from the unit.

( *Myria*—

( *Deca*—  
**Unit.**

Submultiples ... { *Deci*—  
                                  *Centi*—  
                                  *Milli*—

By inserting the *unit* of the particular measure required and prefixing the *Greek* terms *Deca*, *Hecto*, *Kilo*, *Myria*,

you have its multiples by 10, 100, 1,000 and 10,000 respectively. In a similar manner, by prefixing the *Latin* terms *Deci*, *Centi*, *Milli*, you have its submultiples, or one-tenth, one-hundredth, and one-thousandth part of the particular unit employed.

For example: if we insert *gram* for unit in this table, we may write its multiples thus—beginning at the unit and reading up—

Myriagram,  
Kilogram,  
Hectogram,  
Decagram

**gram,**

Similarly we write the scale of sub-division thus—beginning at the unit and reading down—

**gram,**  
Decigram,  
Centigram,  
Milligram,

and so on with the other units.

As an example of the advantage of this system when compared with the old English one, let it be required to calculate the number of milligrams in a myriagram. The term myriagram at once tells us that it contains 10,000 grams; again the name milligram indicates the  $\frac{1}{1000}$ th part of a gram; hence  $10,000 \times 1,000 = 10,000,000$  is the number of milligrams in a myriagram.

Take a similar example and work it by the English system. Let it be required to find how many grains are in one ton. For this purpose you have to multiply by 20 to get cwts., then by 4 to get quarters, and quarters by 28 to get pounds, pounds by 16 to get ounces, ounces by 16 to get drams, and drams by  $27\frac{1}{4}$  to get grains. The task

indicated by these successive multiplications is enough to frighten the most profound mathematician ; and though it may be accomplished in five or ten minutes by a smart boy, yet how many mistakes is he liable to make before he arrives at the correct answer !

As these measures (though employed in all modern books on Chemistry and Physical Science) have not yet come into general use, it will be necessary, until they are actually made compulsory, to be able to convert them into their old English equivalents when you want to get some fixed ideas as to their meaning. But now that we have the weights and measures of the Metric System before us on the table, we can, by the aid of our senses, form fixed ideas as to their actual size ; for instance, we see that a *Liter* (=1.76 pints), the full of which of water at 4° C. weighs a kilogram (=2½ lbs.), does not differ very much from the Poona *Seer*.

The following are the English equivalents of the Metric units :—

Are	= 119.60333 sq.yds.	= 0.0247 acre.
Liter	= 61.02705 cub. in.	= 1.76077 pints.
Gram	= 15.43234 grains	= 0.002205 lbs. (avoir.)
Stere	= 1 cubic meter	= 35.3171 cubic feet

From these values of the several units it follows that—

20 Meters = 65.618 ft., or very nearly *one chain*.\*

1 Hectare = 2.47 acres = 2½ (q. p.) †

1 Hectoliter = 22 gallons

1 Kilogram = 2.205 lbs. (avoir.)

1 Kilometer = 0.6214 of a mile = ⅔ (q. p.)

64 Meters = 70 yards (q. p.)

1 Meter = 1.09 yards, or (q. p.) 1.1.

1 Sq. Meter = 1.196 sq. yards, or (q. p.) 1.2.

1 Cub. Meter = 1.356 cub. yds. or (q. p.) 1.3.

\* One Gunter's chain or 66 feet = 20.12 meters.

† Stands for 'quam proxime,' signifying as near as possible.

Hence for *rapid approximation* we may use the following:—

*Rule*—Multiply meters by 1·1 to get yards.

Multiply sqr. meters by 1·2 to get sqr. yards.

Multiply cub. meters by 1·3 to get cub. yards.

Also we have—

$$\begin{cases} 1 \text{ Inch} & = 2\cdot54 \text{ centimeters (q. p.)} \\ 1 \text{ Sq. Inch} & = 6\cdot45 \text{ sq. } " " \\ 1 \text{ Cub. Inch} & = 16\cdot386 \text{ cub. } " " \end{cases}$$

50·8 kilograms = 112lbs. = 1 cwt.; and 1 grain = 0·0648 gram.

The thermometer we use, in conjunction with the Metric System, is that of Celsius, otherwise called the *Centigrade* thermometer, from the manner in which it is graduated.

This thermometer is so graduated that when it is immersed in melting ice the top of the mercury column stands at 0°, or *zero*, and the degrees below this point are indicated by a *minus* sign: thus — 20° signifies 20 degrees below zero.

That point on the stem at which the top of the mercury stands when the thermometer is immersed in *steam* issuing from boiling water (while the barometer reads 760 millimeters) is marked 100°.

The same space (or that between the freezing and boiling points) on the Fahrenheit scale is divided into 180 degrees. (See Fig. 1.) Consequently a degree centigrade =  $\frac{180}{100} = \frac{9}{5}$ ths of a degree Fahrenheit.

The point marked 0° on the Centigrade corresponds with 32° on the Fahrenheit thermometer. Hence if we wish to convert Fahrenheit degrees into Centigrade,



Fig. 1.

we must subtract 32 from the number of Fahrenheit degrees, before converting them into their equivalent in Centigrade degrees; and *conversely*, we must add 32 to whatever number be found, when we convert Centigrade degrees into Fahrenheit. Hence we derive the following :—

#### RULES.

*1st.*—To convert any number of degrees Fahrenheit into an equivalent number of Centigrade degrees—*Subtract 32 from the number (F) and multiply the remainder by  $\frac{5}{9}$ .*

*Example.*—Let it be required to convert 122° Fahrenheit into its equivalent in Centigrade degrees—

$$122 \text{ less } 32 = 90$$

$$90 \times \frac{5}{9} = 50^{\circ} \text{ Centigrade.}$$

*2nd.*—To convert any number of degrees Centigrade into its equivalent in Fahrenheit degrees.—*Multiply the number (C) by  $\frac{9}{5}$  (or 1·8), and to the product add 32.*

*Example.*—Let it be required to convert 95° Centigrade into its equivalent in Fahrenheit degrees—

$$95 \times 1\cdot8 = 171$$

$$171 + 32 = 203^{\circ} \text{ Fahrenheit.}$$

Centigrade degrees are easily converted into Fahrenheit (*mentally*) by the following :—

**RULE.**—*Double the number of degrees (C), deduct one-tenth of this, and to the remainder add 32.*

$$\begin{aligned} \text{Thus } 50^{\circ} \text{ C} &= (100 \text{ less } 10 \text{ plus } 32) \\ &= (90 + 32) = 122^{\circ} \text{ F.} \end{aligned}$$

Also

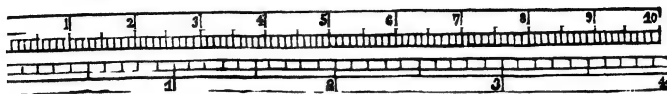
$$\begin{aligned} -40^{\circ} \text{ C} &= (-80 \text{ less } -8^* \text{ plus } 32) \\ &= (-72 + 32) = -40^{\circ} \text{ F.} \end{aligned}$$

Therefore both scales read the same at 40 degrees below zero, on either thermometer.

\* To be subtracted *algebraically*.

# FRENCH AND ENGLISH MEASURES.

A DECIMETRE DIVIDED INTO CENTIMETRES AND MILLIMETRES.



4 Inches divided into tenths.

## METRIC MEASURES IN EQUIVALENT ENGLISH MEASURES.

### MEASURES OF LENGTH.

- 1 Millimetre = 0·03937079 inch, or about  $\frac{1}{25}$  inch.
- 1 Centimetre = 0·3937079 inch, or about 0·4 inch.
- 1 Decimetre = 3·937079 inches.
- 1 Metre = 39·37079 inches = 3·281 feet nearly.
- 1 Kilometre = 39370·79 inches.

### MEASURES OF AREA.

- 1 sq. millimetre = 0·00155006 sq. inch.
- 1 sq. centimetre = 0·155006 sq. inch.
- 1 sq. decimetre = 15·5006 sq. inches.
- 1 sq. metre = 1550·06 sq. inches, or 10·764 sq. feet.

### MEASURES OF VOLUME.

- 1 cub. centimetre = 0·610271 cub. inch.
- 1 cub. decimetre = 61·0371 cub. inches.
- 1 cub. metre = 61027·1 cub. inches.

The litre (used for liquids) is the same as the cubic decimetre.

### MEASURES OF WEIGHT.

- 1 Milligramme = 0·015432349 grain.
- 1 Centigramme = 0·15432349 grain.
- 1 Decigramme = 1·5432349 grains.
- 1 Gramme = 15·432349 grains.
- 1 Kilogramme = 15432·349 grains, or 2·2 lbs. nearly.

### COMBINED UNITS.

- 1 Gramme per sq. centimetre = 2·048098 lbs. per sq. foot.
- 1 Kilogramme per sq. metre = 0·2048098     "     "
- 1 Kilogramme per sq. millimetre = 2·048098     "     "
- 1 Kilogramme-metre = 7·23314 foot-pounds.
- = 7½ foot-pounds nearly.

1 force de cheval = 75 kilogrammetres per second, or 542½ foot-pounds per second nearly; 1 horse-power (English) = 550 foot-pounds per second, or 33,000 foot-pounds per minute.



## EQUIVALENTS OF ENGLISH MEASURES. [CHAP. I.

### ENGLISH MEASURES IN EQUIVALENT METRIC MEASURES.

#### MEASURES OF LENGTH.

- 1 inch = 25·39954 millimetres.
- 1 foot = 0·304794 metre.
- 1 yard = 0·9143834 metre.
- 1 mile = 1·60932 kilometre.

#### MEASURES OF CAPACITY.

- 1 pint = 0·5676 litre.
- 1 gallon = 4·5410 litres.
- 1 bushel = 36·3281 litres.

#### MEASURES OF AREA.

- 1 sq. inch = 645·137 sq. milli'tres.
- 1 sq. foot = 0·0929 sq. metre.
- 1 sq. yard = 0·83609 sq. metre.
- 1 sq. mile = 2·59 sq. kilometres.

#### MEASURES OF VOLUME.

- 1 cub. inch = 16386·6 cub. milli'tres.
- 1 cub. foot = 0·0283 cub. metre.
- 1 cub. yard = 0·7645 cub. metre.

#### MEASURES OF WEIGHT.

- 1 grain = 0·064799 gramme.
- 1 oz. avoird. = 28·3496 grammes.
- 1 lb. avoird. = 0·4535 kilogramme.
- 1 ton = 1·01605 tons.  
= 1016·05 kilog.

#### COMBINED UNITS.

- 1 lb. per sq. foot = 4·88261 kilog. per sq. metre.
- 1 lb. per sq. inch = 0·0703 kilog. per sq. centimetre.
- 1 foot-pound = 0·1382 kilogrammetre.

**N. B.**—For Exercises on the Metric System the student is referred to the Chemical Gymnasium at the end of this Volume.

## CHAPTER II.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

Chemistry is that branch of Experimental Science which has for its object the determination of the composition and properties of the different varieties of matter with which man is acquainted, and of their actions and reactions with one another.

Though Heat, Light and Electricity do not lie within the strict limits of our subject, yet a knowledge of the operations and effects of these physical agents on matter is of prime importance to the Chemist; consequently, in the course of study which we have set before us, it will be necessary to make frequent reference to the phenomena exhibited by such agents.

Modern Physics teaches that Heat, Light and Electricity are but so many forms of *undulatory motion*. Just as Sound is produced by the vibrations of air, so Heat, Light or Electricity may be produced by rapid vibratory motions of material particles.

Heat, Light and Electricity are *transmitted* by wave-like vibrations of an imponderable elastic *ether*, which (there are good reasons for believing) fills all space and the pores which exist in all bodies, in whatever state they may be.

All known forms of matter have *weight* (a term relative to the force of gravity) and *impenetrability* which means that property of a body which enables it to occupy a certain space, and to prevent the portion of space in which it rests from being occupied by any other body at the same time with itself; for example, I take a cube of fluor

sp̄ar and place it on the table before your eyes ; now you can see, plainly, that it would be impossible for me to put another cube in the space occupied by the first, without displacing it ; this property of the cube of fluor spar is called impenetrability, and is possessed alike by solids, liquids and gases. Again, all material bodies are *ponderable*, and are thereby distinguished from the ether which permits the transmission of Heat, Light and Electricity, &c.

The development of heat by mechanical action has led to the overthrow of the *material theory*—which supposed heat to be a *subtle imponderable variety of matter*. Gmelin, for instance, says heat is that *substance* whose entrance into our bodies causes the sensation of warmth, and its egress the sensation of cold.

The celebrated chemist Davy was the first to *disprove the materiality of heat*. Davy showed that ice could be liquefied by *mere friction*.

Rumford was the next experimenter in this field of research. He actually boiled about 2 gallons of water (originally at 60° F.) by the friction of boring a brass cylinder immersed in it. The brass cylinder weighed 113 lbs., and the time occupied in bringing the water to the boiling point was 2½ hours. Rumford concluded, from this experiment, that heat must be *motion*.

Heat is now regarded as a 'form of motion,' or rather *molecular vibration*. Thus when a cannon ball is let fall from the top of a tower, its motion *appears to cease* when it comes in contact with the ground ; such, however, is not actually the case, but its *linear motion* is thus converted into a *vibration of its molecules* which is exhibited in an elevation of the temperature of the ball.

Experiments, made in Paris, have proved that water

may be warmed by letting heavy balls fall into it from a considerable height.\*

The stoppage of the motion of carriages, &c., by friction furnishes another illustration of the conversion of direct motion into heat. The 'brakes' on railway carriages occasionally take fire from the heat produced in this way. Heat is also convertible into *direct* and *visible* motion, as in the case of the Steam Engine.

If heat be not a *kind of motion* (viz. *molecular vibration*) it becomes most difficult to explain such phenomena.

All varieties of matter exist in one or other of *three states*, namely, the solid, the liquid† and the gaseous, or aeriform. Some bodies are found in, or can be made to assume, each of the three different states. Water, for instance, is found in nature as a solid (ice) in the Arctic regions, and occasionally in warmer countries, and ice can easily be produced artificially; it is found as a liquid in oceans, seas, rivers, and wells, &c., and in the form of rain falling through the air; as a gas, in the jets of steam issuing from the geysers of Iceland and volcanoes of that and other countries—also in our atmosphere (as vapour), and is produced artificially in the boiler of the steam engine for purposes of locomotion, &c.

The following experiments will show that other substances than water are capable of changing their state:—

Here I have a few fragments of sulphur in a flask. I warm the flask over a spirit lamp, and I continue to do so till (as is the case now) I see its contents become liquid; the sulphur has now changed its former solid for its present liquid form. Let us now observe, what will be

\* It has been even proposed to boil eggs by letting them fall from a great height!!

† An intermediate state called the *viscous* is also recognizable. Gummy and gelatinous substances generally may be said to be in the viscous state.

the effect of a further application of heat to the molten sulphur. Well, you see that the sulphur is now escaping out of the neck of the flask, in the form of vapour; and by inverting another flask over the neck of the first, we can collect the vapour of sulphur in a condensed state in the inverted, or cold, flask. When in this condition it is known as sublimed sulphur.

Here is some sulphuric ether; you see it is in the liquid state, but now I will warm the beaker a little, and you will soon perceive that the liquid will no longer be visible; it will be all converted into vapour at  $36^{\circ}$  C. You see now the vessel is apparently empty; the presence of its vapour, however, may be shown thus:—I bring this lighted taper just over the beaker; and there! you see the gaseous ether burst into flame. If, instead of heating the liquid ether, I were to cool it sufficiently, it would become a solid, having the appearance of camphor.

I throw these few grains of iodine into this large flask and gently heat it; now observe the flask is filled with a beautiful violet-coloured vapour. In this case the iodine is changed directly from the solid to the gaseous form, without passing through the intermediate or liquid state—such a process is called *sublimation*. The iodine, however, may be liquefied by heating it under greater pressure. There are a few other substances which behave in a similar manner, but, as a general rule, most substances pass through the liquid stage, on their way to the gaseous, from the solid state.

You will have noticed that, in all these experiments, the power employed to do the work of changing the condition of the substance experimented upon was heat. Heat, then, has *power to do work*, and is, therefore, a *form of energy*.

All perceptible masses of matter are considered to be

made up of particles very much smaller than anything we can see. A cannon ball may, by mechanical means, be divided into very small pieces, so small that one piece would be scarcely visible to the naked eye; by chemical means, however, we can bring it to a much finer state of division; for example, let us take one grain of iron, dissolve it in this acid,\* and then add water until the whole solution equals one gallon. Here then is a gallon of solution containing in it one grain of metallic iron, uniformly distributed throughout the water. Now by letting a few drops of another solution (potassium ferrocyanide) fall into the gallon of clear liquid, the whole of it instantly becomes blue. If we remove  $\frac{1}{100}$ th part of a grain of this coloured solution, and place it on a sheet of white paper, the blue colour of the little drop will be distinctly visible; and as the blue colour of this little speck is due to the presence of a portion of the iron originally contained in the first solution, we have evidently succeeded in dividing a grain of iron into seven million parts, for a gallon of water contains 70,000 grains and  $\frac{1}{100}$ th part of the grain is therefore the one-seven millionth part of a gallon. It is scarcely necessary to say that the quantity of metallic iron in that little drop of blue water ( $= \frac{1}{7,000,000}$ th of a grain) is so indefinitely small as to be perfectly invisible. From considerations of this kind it has been thought that there is no limit to the divisibility of matter, or in other words, that it is *indefinitely divisible*. However, all chemists are opposed to this idea, and the general doctrine taught by them is that *there is a limit* to the divisibility of matter, and when that limit is reached there is left only the *ultimate chemical particles* of which the entire mass is made up. Such ultimate particles, as they are supposed not to admit of

\* Hydrochloric (containing a drop of nitric) acid.

further division, are called *atoms*, from the Greek term *ἄτομος* (atomos), signifying *indivisible*.\*

As we shall have occasion again to refer to the doctrine of atoms, I shall say no more about it until we have studied the laws of combination. It will, however, be convenient, for the purposes of explanation, occasionally to use the term atom as an equivalent for ultimate *chemical* particle.

Large masses of matter, then, may be regarded as composed of aggregations of these particles, or atoms, held together by the mutual attraction of each other and the force of *cohesion*, more properly called *molecular attraction*. Cohesion, or molecular attraction, binds together *groups of atoms*, or molecules,† which again are composed of *simple atoms*, held together by chemical attraction, otherwise called affinity.

Although the molecules of bodies are held together by the attraction of cohesion still they are not in actual contact; the molecules, it is supposed, do not touch each other, but have little spaces, or *pores*, between them. The probability of the truth of this conclusion has been greatly increased by the celebrated *Florentine Experiment*, which has satis-

\* Sir William Thompson has communicated to *Nature* a remarkable paper on the size of atoms, in which he deduces the conclusion that in ordinary liquids or transparent solids the mean distance between the centres of contiguous molecules is less than the hundred-millionth, and greater than the two thousand-millionth of a centimetre.

‘If we imagine (he says) a globe the size of a pea to be magnified to the size of the earth, then each molecule would, on this supposition, be larger than a pellet of small shot, but less in size than a cricket ball. The hypothesis is supported by many convergent considerations, one of which is that a soap bubble probably bursts when it becomes too thin to contain several atoms in its thickness, and as the thicknesses of a soap bubble are known from the nature of the colours reflected, a *limit* is obtained to the maximum size of the atoms composing it.’

† Molecule (*molecula*, a little mass) the smallest quantity of a substance which can exist by itself, is the *physical* particle in contradistinction to the *chemical* particle, or atom.

factorily established the fact that gold is porous. This beautiful experiment was undertaken by the Florentine academicians for the purpose of trying whether water was compressible or not. They filled a hollow globe of gold with water, and having hermetically sealed it, they subjected it to great external pressure, knowing (from the mathematical properties of the sphere) that if it changed its shape at all in yielding to the pressure, the water must have contracted in bulk, and consequently be compressible; however, it was found that, without solving the problem in question, the water came through the gold and appeared like dew-drops on its external surface.

From the result of this experiment it is evident that gold is porous, and if such a dense body as gold be porous, it is not difficult to believe that other bodies may be so too.\* The facts that most bodies, no matter how dense, can be made more so by hammering and by the reduction of their temperature, are strong arguments in favour of the *porosity of matter*.

If we take a piece of iron or other metal and hammer it briskly on an anvil it will become smaller. Again if we take a metallic ball, and reduce its temperature considerably, it will be found that it will contract in volume, which can be made evident by making it pass through a ring (Fig. 2), through which it would not go before its temperature was reduced.

It has been concluded that the



Fig. 2.

\* Copper and Zinc have recently been shown to be porous, by experiments made at Manchester. Spermaceti oil contained in a brass (*i.e.* a mixture of copper and zinc) cylinder was forced, by pressure, through the pores of the brass, until the cylinder was emptied.



porosity of matter is due to the existence of a *repulsive force* between its particles, which has been called by Philosophers *molecular repulsion*, in contradistinction to *molecular attraction*, or the force of cohesion, which acts in an opposite direction. From experiments of the above nature and a knowledge of the general effects of heat on matter, it is now generally admitted that the force called molecular repulsion by the early Philosophers is *identical* with heat itself. On this hypothesis the phenomenon of change of state is easily explained: for we know that by the aid of heat solids are converted into liquids, and liquids into gases.

In all masses of matter, then, we must admit the existence of two forces, the attraction of cohesion tending to draw the molecules closer together, and heat tending by its action to drive those very same molecules farther asunder. Hence, when matter occurs in the solid state, the force of cohesion overcomes the repulsive force exerted by heat. In the liquid state these two forces exactly balance each other; but in the gaseous condition the repulsive must far exceed the attractive force. Consequently, we may say that *the existence of any body in one or other of the three states—solid, liquid, or gaseous—is solely dependent on the quantity of heat it contains* (pressure being supposed constant).

The quantity of heat absorbed by a body during the process of changing its state is very appropriately called '*Constituent Heat*,' and also '*Latent Heat*,' because this amount of caloric has no effect on a thermometer, and is therefore said to be latent in the substance.

I have here used the term '*quantity of heat*,' and before going further it will be necessary to explain its meaning to you. Although we have no means of measuring the *absolute* quantity of heat contained in any body, yet we

may fix upon some *relative standard*, by which we can compare the different amounts of caloric, or heat, absorbed by different substances. The standard fixed upon is *the quantity of heat necessary to raise the temperature of one kilogram of distilled water through one degree (as measured by the Centigrade thermometer), or from  $0^{\circ}$  to  $1^{\circ}$  C., and is called 'One Degree of Heat.'* And the number of degrees of heat required to raise a kilogram of any other substance through one degree of temperature \* ( $0^{\circ}$  to  $1^{\circ}$  C.) may be called the *Specific Heat* of that substance—referred to water as unity.

Thus a kilogram of hydrogen requires 3.4 times as much heat as the same weight of water, to raise its temperature from  $0^{\circ}$  to  $1^{\circ}$  C., or in other words, a kilogram of hydrogen requires 3.4 degrees of heat to raise its temperature one degree. Hence *the specific heat of hydrogen is 3.4*, that of water being *unity*. Hydrogen, it may be remarked, has an abnormal specific heat, being greater than that of any other known substance.

A kilogram of oxygen requires about  $\frac{1}{8}$ th of a degree of heat to raise its temperature one degree. Hence *the specific heat of oxygen* may be represented by the fraction  $\frac{1}{8}$ th (or more accurately .218). Every substance has its own specific heat, or, as it is sometimes called, '*capacity for heat.*'

Having explained the terms '*quantity of heat,*' '*degree of heat,*' &c., we are now in a better position to understand what is meant by *latent heat*, and are enabled to apply a measure to it.

If a kilogram of water at  $80^{\circ}$  C. be mixed with a kilogram of ice at  $0^{\circ}$  C., after the lapse of a short time, we shall have 2 kilograms of water at the temperature  $0^{\circ}$  C. Here, then, the kilogram of water gives up its 80 degrees of heat to the

\* Care must be taken to distinguish between a degree of heat and a degree of temperature—Temperature indicates the *intensity* of heat in a body, but not the *quantity*.

ice, which absorbs that same amount in becoming water at  $0^{\circ}$  C.—*i.e.* in changing its solid for the liquid state. The temperature of the liquefied ice, you observe, is not altered; it remains  $0^{\circ}$  C. as at first. The 80 degrees of heat, then, which were lost by the water have been absorbed by the ice, in becoming liquid. That amount of heat has been spent in *doing the work* of overcoming the attraction of cohesion, which held together the particles of the ice in the solid state. These 80 degrees of heat, being insensible to the thermometer, are said to be *disguised*, or latent.

The quantity, or number of degrees, of heat absorbed, or rendered latent, by a kilogram of ice at  $0^{\circ}$  C. in becoming water at  $0^{\circ}$  C., is called the *latent heat of liquefaction of water*, or the *latent heat of ice*, and sometimes the *caloric of liquidity*.

From the result of the foregoing experiment it appears that the latent heat of ice is  $80^{\circ}$ —*i.e.*, it requires 80 *thermal units* to reduce a kilogram of ice at  $0^{\circ}$  C. to a kilogram of water at the same temperature.

*A thermal unit, a unit of heat, and a degree of heat*, are but three different modes of expressing the quantity of heat required to raise a kilogram of water through one degree of temperature.

We can also measure the latent, or constituent, heat of *steam*, *i.e.* the quantity (measured in thermal units) of heat absorbed by a kilogram of *water* at  $100^{\circ}$  C. in becoming *steam* at  $100^{\circ}$  C., or, which is the same thing, the quantity of heat given out, or evolved, by a kilogram of *steam* at  $100^{\circ}$  C. in becoming *water* at the same temperature. As this amount of heat is insensible to the thermometer, we must resort to other means of measuring it.

A very simple method of determining this important element may be thus described in the words of Professor Williamson :—

'Put  $5\frac{1}{2}$  kilograms of ice-cold water into a jar, and blow steam into it till no more can be condensed. Then weigh the boiling hot water thus obtained. The first portions of steam condense ~~to~~ water and are cooled by mixing with the ice-cold water; but at the end of the experiment the original  $5\frac{1}{2}$  kilograms of water, together with the water formed by the condensation of the steam, are left at the temperature of  $100^{\circ}$  C.; so that the steam may be considered to have been condensed without becoming cooler, and to have evolved  $5\frac{1}{2} \times 100 = 533^{\circ}$  of heat by its condensation. The increase of weight is nearly one kilogram; so that a kilogram of steam condenses to water of the same temperature evolving about  $533^{\circ}$  of heat.'

Hence we may say that the *latent heat of steam* is represented by about 533 degrees of heat. More exact experiments have recently been made by Regnault, from which it is deduced that the latent heat of steam = 537 units.

Regnault has further given the following empirical formula for the *total quantity of heat necessary for the evaporation of a kilogram of water at any temperature* :—

$$\text{Total Heat} = 606.5 + 0.305t.$$

Using this formula, we find that the total quantity of heat in a kilogram of steam at  $100^{\circ}$  C. is  $606.5 + .305 \times 100 = 637$ . Hence by subtracting the sensible heat (*i.e.*  $100^{\circ}$ ) we have, for the latent heat of steam, *raised at*  $100^{\circ}$  C. the number 537.

It has been ascertained that a kilogram of air, oxygen, hydrogen, or any other perfect gas requires *more heat* to raise its temperature  $1^{\circ}$  if the gas be allowed to expand while it is being heated than when its volume is not allowed to increase during the application of heat: hence the specific heats of gases under a *constant pressure* are greater than their specific heats at a *constant volume*.

If we call the specific heat of a gas at a constant volume 1, then its specific heat at a constant pressure, but increasing volume, will be represented by 1.413, or the ratio of the specific heats in the two cases is 1 : 1.413.

You will very naturally ask the question why should air require more heat to increase its temperature  $1^{\circ}$  when it is free to expand than it would were it shut up in a bottle for instance?

Well, that question is easily answered :

Let us now suppose that we have a liter of air in this bottle, and another liter of air in this long tube. You can fancy the air confined in the lower part of the tube, and prevented from mixing with the rest of the atmosphere, by a piston exactly fitting the tube. The piston may be supposed to be without weight, for the purpose of explanation. I am sure you all know (if not, you ought to know) that *the atmosphere has*

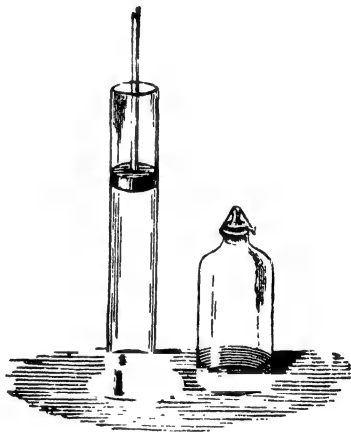


Fig. 3.

*weight*, and that it presses down on all bodies at the surface of the earth with a pressure of nearly 15 lbs. (14.7) on every square inch of surface, or 10.333 kilograms per square meter. Now, imagine the same amount of heat to be applied to each vessel; the air in the bottle has nothing else to do with the heat it receives but *warm itself*; whereas the air contained in the open tube in expanding has to *lift* the weight on the back of the piston,

caused by the pressure of the column of atmosphere directly over it, and for this purpose it *takes the force necessary for moving that weight from the heat, leaving the remainder to warm the liter of air*. Now you can answer the question by saying, that some of the heat is spent in doing the work of lifting the weight caused by the constant atmospheric pressure.

Here I give you a table of the specific heats of some of the common metals. These numbers are very useful, and some of them should be remembered :—

Metallic Names.		Specific Heats.
Water = 1.	Iron .....	0·11379
	Zinc .....	0·09555
	Copper .....	0·09515
	Silver .....	0·05701
	Lead .....	0·03140
	Bismuth .....	0·08084
	Platinum .....	0·03243
	Gold .....	0·03244
	Mercury (solid) .....	0·03195

In this table the *standard* referred to is the *specific heat of water*, which is taken as *unity*. We see by these numbers, each of which is less than unity, that it is more difficult to warm or to cool a given quantity of water than the same quantity of any of those substances mentioned in the list. Hence the great value of water, as a *heat-storer*, for domestic and culinary purposes.

It has been shown by Mr. Joule, of Manchester, that if the force which is *stored up* in one degree of heat be applied to do mechanical work (such as lifting weights), it would be found equivalent to 423·6 *meter kilograms of work*, that is, it would be sufficient to raise 1 kilogram weight to a height of 423·6 meters, or (which is the same amount of work) 423·6 kilograms to a height of 1 meter.

Now the *unit of work* (in the Metric System) being a kilogram lifted to a height of 1 meter, the *mechanical equivalent* of one degree of heat is, therefore, equal to 423·6 (or in round numbers 424) units of work. Hence we see that a kilogram of steam, in condensing to water, would yield  $537 \times 424 = 227,688$  units of work. This gives us a fair idea of the great amount of work obtainable from a small quantity of steam.

It also follows that if a kilogram of water be let fall from a height of 424 meters, its temperature would be raised one degree. If a kilogram weight of any other substance (than water) be let fall from this height, its temperature would be raised  $1^\circ \times$  the reciprocal of the specific heat of that substance, assuming that all evolved heat were stored up in the falling body,\* which, of course, would not be accurately true, as some of the heat would be imparted to the body fallen against.

\* Thus, the specific heat of iron being  $\frac{1}{9}$ , a kilogram of iron falling 424 meters would have its temperature raised 9 degrees, if all the evolved heat were stored in the iron.

## CHAPTER III.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

The matter of which the world is composed is, you all know, not one uniform substance, such as a lump of lead, but is made up of different materials; and these materials are either simple or compound.

Bodies which cannot be separated, or decomposed, into two or more different kinds of matter are called *Simple Substances*, or *Elements*.

All those bodies, which can be resolved into two or more different varieties of matter are, very properly, termed *Compound Substances*.

The simple bodies, or elements, may be called the letters, and the compound substances, being composed of two or more simple ones, the words, of chemistry.

Silver, for example, is an element, as it cannot be resolved into anything else but Silver. Silver, then, represents a chemical letter.

Salt, being decomposable into the elements sodium, a metal, and chlorine a gas, represents a chemical word composed of two letters. We seldom find any chemical words containing more than six letters, so that you ought not to find it difficult to read our chemical language after a little study.

The elements are divided into two classes—*metals* and *non-metals*—the latter being also called *metalloids* (metal-like). The former class are generally distinguished from the latter by certain properties which are possessed in a high degree by the metals, but are never found united in the non-metallic elements.



Such properties are those of conducting heat and electricity, and the power of reflecting light, so as to give the appearance called *metallic lustre*. In addition, the metals may be said, generally speaking, to have what is termed the *metallic ring*, *i.e.* the ringing noise which is heard when we let a piece of metal, a coin for instance, fall on a flagstone or strike it with a hammer.

Many of the metalloids possess in a less degree some of the properties just mentioned. Another distinction (and an important one) between the metals and the non-metals is that the former are *electro-positive*, while the latter are *electro-negative*, elements.

I must now explain to you the sense in which these terms are to be understood. You know, I suppose, that before the terminal wires of a galvanic battery are brought together, *i.e.* before contact is made, the one pole or extremity of the wire is in the positive, and the other in the negative, electric condition; and that the current passes when the wires are brought into contact.

Now if, instead of bringing the wires into actual contact, we interpose an *electrolyte* (which is a compound that can be decomposed by an electric current passing through it) and make contact by inserting each terminal wire in the electrolyte, when the current passes this compound substance will be decomposed into its constituents; and it is observed that certain of those constituents invariably appear at the positive, and others at the negative, pole of the battery.

Therefore, on the well-known principle that bodies *oppositely* electrified attract each other, those constituents which constantly make their appearance at the *positive* pole are said to be *electro-negative*, and those which constantly appear at the *negative* pole are called *electro-positive*.

For example, if we *analyse* (or resolve into its constituents) water, by the aid of a galvanic current, we invariably find that hydrogen is set free at the negative, and oxygen at the positive, pole. Hence hydrogen is regarded as an electro-positive, and oxygen as an electro-negative, body.

Hydrogen, which behaves like the metals, is now very generally believed to be a metal in the gaseous state.

About sixty-nine or seventy elements, or simple bodies, have already been discovered.\* Many of them are still very scarce, being only obtainable in such minute portions that their value and use in the arts have not yet been fully ascertained. Of these seventy bodies about four-fifths are metals and one-fifth metalloids.

The names assigned to these elements are, in many instances, of Latin origin. Some of them are designated by names indicative of some peculiar property which they may happen to possess : for instance, chlorine is so called from a Greek word, *chloros*, signifying green, it being a greenish-coloured gas.

We use a kind of short-hand in writing the names of the elements ; the first letter of the name serves to indicate some ; a second distinguishing letter is added, when more than one element begins with the same letter. These abbreviations are called *Chemical Symbols*.

The names and symbols of some of the most frequently-occurring elements must be carefully committed to memory.

Here is a list of the elements, arranged in alphabetical order, and in column (3) you will find their chemical symbols :—

\* Several of these have recently been discovered by the aid of the 'Spectroscope,' and it is probable that the *Spectrum Analysis* of the heavenly bodies will add considerably to the list of elementary substances. It is, moreover, possible that some of the substances, now regarded as elements, may, through the aid of improved means of research, prove to be subtle compounds. Nitrogen, Sulphur and Chlorine, for example, are already suspected to be compound bodies.

TABLE A,

*Showing the names and symbols of the Elements.*

(1)	(2)	(3)	(1)	(2)	(3)
Name.	Latin Name.	Sym- bol.	Name.	Latin Name	Sym- bol.
Aluminum ..	....	Al.	Molybdenum	....	Mo.
Antimony....	Stibium ....	Sb.	Nickel.....	....	Ni.
Arsenic	....	As.	Niobium....	....	Nb.
Barium.....	....	Ba.	Nitrogen....	....	N.
Bismuth	....	Bi.	Osmium ....	....	Os.
Boron	....	B.	Oxygen	....	O.
Bromine	....	Br.	Palladium ..	....	Pd.
Cadmium	....	Cd.	Phosphorus..	....	P.
Cæsium.....	....	Cæ.	Platinum ..	....	Pt.
Calcium	....	Ca.	Potassium ..	(Kalium) ..	K.
Carbon	....	C.	Rhodium	....	R.
Cerium	....	Ce.	Rubidium ..	....	Rb.
Chlorine	....	Cl.	Ruthenium	....	Ru.
Chromium ..	....	Cr.	Scandium ..	....	Sc.
Cobalt	....	Co.	Selenium ..	....	Se.
Copper	Cuprum ....	Cu.	Silicon	....	Si.
Decipium ....	....	De.	Silver	Argentum.	Ag.
Didymium ..	....	D.	Sodium	(Natrium).	Na.
Erbium	....	E.	Strontium ..	....	Sr.
Fluorine	....	F.	Sulphur	....	S.
Gallium	....	Ga.	Tantalum ..	....	Ta.
Germanium..	....	Ge.	Tellurium	....	Te.
Glucium....	....	G.	Thallium	....	Tl.
Gold	Aurum ....	Au.	Terbium....	....	Tr.
Hydrogen...	....	H.	Thorium....	....	Th.
Indium	....	In.	Tin	Stannum	Sn.
Iodine	....	I.	Titanium	....	Ti.
Iridium.....	....	Ir.	Tungsten (or		
Iron	Ferrum ....	Fe.	Wolfram)..	....	W.
Lanthanum ..	....	La.	Uranium	....	U.
Lead	Plumbum, ..	Pb.	Vanadium ..	....	V.
Lithium	....	Li.	Yttrium	....	Y.
Magnesium ..	....	Mg.	Ytterbium..	....	Yb.
Manganese	....	Mn.	Zinc	....	Zn.
Mercury	Hydrargyrum	Hg.	Zirconium ..	....	Z.

The names of most of the metals have been made to terminate in *um*, as Platinum, Aluminum, &c., in order to

correspond with the terminations of the Latin names of those known to the ancients.

With the exception of Selenium and Tellurium, the names of none of the metalloids end in 'um.' Selenium and Tellurium, though considered by many chemists to be metals, are sometimes classed with the metalloids, and may continue to be so until we obtain more conclusive evidence to the contrary than at present exists. The chemistry of these elements is usually considered in conjunction with sulphur; that of Arsenic with the Metals.

The following table gives the names and symbols of the elements commonly known as metalloids, or non-metallic elements :—

TABLE B,

*Showing the names and symbols of the Non-Metallic Elements.*

Name.	Symbol.	Condition at ordinary atmospheric temperatures.
1. Oxygen.....	O.	Gaseous.
2. Nitrogen .....	N.	"
3. Chlorine .....	Cl.	"
4. Fluorine .....	F.	"
5. Bromine .....	Br.	Liquid.
6. Iodine .....	I.	Solid.
7. Carbon.....	C.	"
8. Boron .....	B.	"
9. Silicon .....	Si.	"
10. Phosphorus .....	P.	"
11. Sulphur .....	S.	"
12. [Selenium] .....	[Se.]	"
13. [Tellurium] .....	[Te.]	"
14. [Arsenic] .....	[As.]	" } Semi-metallic.

Now, having given you the symbols for the elements, before we go further, let me impress on your memory the

fact that these symbols stand for something more than mere abbreviations for the names themselves. Each symbol represents a certain proportion, or number of parts by weight, of the element it stands for, and not the element itself in the general, or abstract, sense.

As an illustration, I may tell you that O does not stand for the term Oxygen in general, but for 16 parts by weight of Oxygen; so also H stands for 1 part by weight of Hydrogen: and so on with the other elements. The numbers representing these proportions, or parts by weight, are commonly called *combining proportions*, or *atomic weights*.

The term *chemical equivalent* was formerly used synonymously with atomic weight. In modern Chemistry, however, it is necessary to distinguish between these ideas. Two quantities of different bodies can only be said to be *equivalent* to each other when they can *replace* each other in combination, and the proportions in which bodies thus replace each other are, properly speaking, their *equivalent proportions*. Some bodies, too, such as iron, mercury, &c., have two equivalents, although they can have but one atomic weight.

A fuller explanation of this subject will be given in a future lecture (Chapter IX.).

The great mass of the earth's rocky crust is composed of but a limited number of the elements. According to a rough estimate, the following list represents the average percentage composition of the crust of the earth:—

Oxygen.....	48
Silicon .....	29
Aluminum .....	8
Iron .....	6
Calcium .....	3
Magnesium .....	2
Sodium .....	2
Potassium .....	1·5
Hydrogen.....	0·2
Remaining Elements ....	0·3

## CHAPTER IV.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

In the last lecture we learned that a compound substance was one which could be resolved into two or more simple ones.

This statement naturally suggests the inquiry : Can we not make compound bodies by mixing together two or more simple ones? The question admits of an affirmative answer, but as the mere mixing of bodies is *not always* sufficient to cause them to unite chemically, we had better now consider *the conditions necessary for combination.*

One of the most important of those conditions is that *chemical attraction*, or *affinity*, should exist between the simple bodies brought together. By affinity you are to understand the force by virtue of which two or more simple atoms combine to form a compound atom, or molecule.

‘Molecule is the name given to the *smallest cluster of atoms* of any substance, whether an element or a compound, that is believed capable of existing by itself; and every pure compound consists of similar molecules.’

Affinity, or chemical attraction, differs from the attraction of gravitation (the force of gravity), and from cohesion in many respects. The force of gravity operates at all, *even the greatest distances*, while chemical affinity and the attraction of cohesion operate only at *insensible distances*.\*

Affinity is to the chemist what gravity is to the student of mechanics, ‘the most important of the forces active in nature.’

The attraction of gravitation is the power by virtue of which matter attracts matter; it is exerted by all masses

\* *i.e.* distances so short as to be imperceptible to the senses.

of matter, however large: 'it is the invisible, yet insuperable, tie which, connecting together the satellites and planets of our system with the central sun, assigns to each of the tenants of our boundless skies its place and motions.'

The downward pressure caused by the exercise of this attractive force on any body within the earth's 'sphere of attraction' is called the *weight* of that body.

Molecular attraction, or cohesion, may be considered as the force by the exercise of which the individual molecules of bodies are held together.

The differences between these three attractive forces are exhibited in the following table:—

TABLE C,

*Showing the differences between gravity, molecular, and chemical attraction.*

Attraction of Gravitation	is exerted by every variety and by all masses of matter of whatsoever dimensions, and at all distances.
Molecular Attraction, or Cohesion,	is exerted, generally, by molecules of the same kind; no new properties are found in the aggregations of matter formed by its influence, and it acts only at insensible distances.
Chemical Attraction, or Affinity,	is exerted, generally, by atoms of different kinds*; the compounds formed by its influence possess properties different from those of its constituents; it acts only on <i>definite</i> proportions of matter, and only at insensible distances.

\* The molecules of an element are composed of atoms of the same kind, held together by the bond of affinity.

I cannot better illustrate the distinctions between molecular attraction and affinity than by quoting the words my revered teacher, the late Professor Apjohn :—

‘ If a crystal of Iceland spar be struck with a hammer, breaks up into two or more fragments. The force which previously held the fragments in juxtaposition, and which has been overcome by the mechanical violence employed, is molecular attraction. If now one of these fragments be thrown into a little nitric acid, a gas known to exist under the name of carbonic acid, escapes ; and hence, the second proximate constituent of the spar, entering into union with the nitric acid, gives rise to the production of the salt called nitrate of calcium. The force which held the carbonic acid of the spar in union with lime, and which has been overcome by the intervention of the nitric acid, is chemical affinity. Though quite distinct, these forces are nevertheless very intimately related in one important particular, viz. that *whatever increases the energy of cohesion promotes the action of affinity*. Hence heat and solvents, which diminish the cohesion of solids, invariably favour their chemical action on each other. Sulphur and copper, when mixed, do not combine till heat is applied ; and dry nitrate of copper, when read upon tinfoil, exerts upon it no chemical action till a little of the former is dissolved by the addition of a few drops of water, when the oxidation of the metal is readily accomplished, and with the phenomena of combination.’

Some philosophers consider that the ‘ attraction of adhesion,’ by virtue of which small particles of matter, such as dust, adhere to the walls of our houses and to our clothing, is identical with cohesion, or molecular attraction. As adhesion and its laws belong rather to the study of mechanics than to that of chemistry, we shall leave the full explanation to the teacher of the former science.



and proceed to consider other conditions necessary for combination; and for that purpose I must ask you carefully to observe the following experiments.

I take a small piece of phosphorus and dry it in this blotting paper. Now I have put the phosphorus into this bent spoon. I ignite it in the lamp, and then introduce the spoon into this glass jar, which is ready filled with oxygen.

Now observe the result! The phosphorus bursts into a very brilliant flame, which is due to the heat evolved by the combination of the phosphorus with the oxygen.

The compound thus formed appears like white smoke, which precipitates on the sides of the jar, and finally falls down into the water below, forming with it a solution of phosphoric acid.

Now I shall perform a similar experiment, using chlorine instead of oxygen. The jar is now full of chlorine; in this case I dry a small fragment of phosphorus, as before, and cut it into little pieces, but I do not ignite it previously to introducing it into the jar of chlorine. Observe the result. The phosphorus takes fire and bursts into a flame of yellowish-green colour. The compound produced by the combination of the phosphorus and chlorine is called chloride of phosphorus. Phosphorus and iodine also combine without heating, forming iodide of phosphorus.

We conclude from these experiments that the *temperature at which combination takes place is not the same for all substances*. The chlorine and phosphorus combined without the aid of a higher temperature than that of the atmosphere; whereas the oxygen and phosphorus required to be heated, by igniting the phosphorus, before they entered into rapid combination. Hence we may say, that a *certain temperature (varying with the substance) is*

*a necessary condition for the combination of different substances.*

Experiments like those just performed might easily be multiplied, but as we shall have more of them when studying the chemistry of the different elements, I shall now only draw your attention to one more experiment in illustration of the fact that a certain definite temperature is a necessary condition for the combination of bodies.

‘Place in a beaker, or other convenient glass vessel, a piece of phosphorus, and half-fill the vessel with water. Fill a bladder, which is fitted with a stop-cock and bent tube, with oxygen, and direct a stream of gas upon the phosphorus. When the two elements come in contact the phosphorus will not burst into flame; increase the temperature of the water ten degrees and then direct the stream of oxygen upon the phosphorus. Continue to increase the temperature of the water ten degrees, after each occasion that the oxygen has been directed upon the phosphorus, until the phosphorus bursts into flame when the two elements are brought into contact. When this takes place, the temperature of the water will be about 145° F.’—(Galloway).

The chemical combination of two or more bodies is frequently attended with an evolution of heat, light or electricity.

You observed that when phosphorus was made to combine with oxygen, by heating the phosphorus to the temperature at which rapid combination takes place, more heat and light were evolved than were imparted to the phosphorus in the first instance by the flame of the lamp. The light evolved was almost dazzling. A certain initial temperature is necessary in order to make phosphorus and oxygen begin to combine (by rapid combustion), and

the amount of heat necessary for its continuance (and in this case more than sufficient for that purpose) is evolved during the act of combination. Hence once combustion of the phosphorus in oxygen is started we do not need to apply further heat.

You will probably ask, are there any instances in which the heat evolved during the combination of substances is *insufficient* (without the application of external heat) to continue the act of combination?

Well, there are: but instances of this kind rarely occur. There is one very remarkable case of this nature which deserves to be noticed, inasmuch as it is not only a good example of its kind, but also teaches us to admire the wisdom of the Creator in providing conditions suitable to our nature.

It is a well-known fact that nitrogen and oxygen do not combine under ordinary circumstances; it would, indeed, be bad for us if they did, since, by so doing, they would deprive us of one of the essential conditions of life, viz. the *free oxygen* in the atmosphere.

The atmosphere, as you will presently learn, is composed of a mixture of oxygen and nitrogen, not in chemical combination, but a mere mechanical mixture. Now, when a portion of the atmosphere is confined in a vessel and electric sparks passed through it, the oxygen and nitrogen combine, forming acid vapours,\* to inhale which, even in small quantities, is most injurious to the human system, and were the whole atmosphere converted into these acid vapours, our life would become extinct.

But (according to Dr. Frankland) the temperature at which combination takes place between nitrogen and oxygen is about  $3000^{\circ}\text{C}$ . The temperature produced by the combustion of oil, gas, candles, fires, &c., is con-

\* Consisting of gaseous nitric and nitrous acid.

siderably below this, and therefore *insufficient* for the combination of the two gases under consideration.

The temperature of the electric spark, however, we have said, is sufficiently high to determine their combination, so also is the temperature of the oxy-hydrogen flame (about 7000° C.).

Why is it, then, that neither the lightning discharge nor the oxy-hydrogen flame can 'set the air on fire,' *i.e.* make its constituents, oxygen and nitrogen, combine to form those acid vapours which would destroy our lives?

Here is the secret! Because *the heat evolved by the combination of nitrogen and oxygen is insufficient to continue the act of combination*, or, in other words, although we can, as it were, set fire to the air by the flame of the oxy-hydrogen blow pipe, in consequence of the heat produced by the combustion of nitrogen and oxygen being less than what is required for their chemical union, the combination of these gases cannot be propagated from particle to particle, but is confined to those particles in immediate contact with the flame.

The same reasoning may be applied, *mutatis mutandis*, with regard to the electric discharge.

You can now understand why our atmosphere is not converted into nitric acid during a thunderstorm, and can admire the Infinite wisdom displayed in the selection of the constituents of the air we breathe.

Were the nitrogen of the atmosphere replaced by another gas, hydrogen for example, what would become of us? The first attempt to light a fire, candle, or other combustible material would cause the atmosphere to take fire and explode with such sudden violence as to kill all the inhabitants of the earth; and even if we could survive the shock we would afterwards be suffocated by the remaining hydrogen, for  $\frac{2}{5}$ ths of the atmosphere would

thus be converted into water, the remaining  $\frac{2}{3}$ ths, being hydrogen, would very soon put an end to our existence.

Thousands have lost their lives by bringing a lighted candle or lamp into an *explosive atmosphere*, such as is often met with in coal mines. A gas known to chemists by the names *Marsh Gas* and *Light Carburetted Hydrogen* is frequently formed in coal mines; it issues out of fissures in bituminous coal, and mixes with the air in the mine. This gas will burn in contact with air with a pale *blue light*, although, if a lighted taper be immersed in a jar of it, the taper will be extinguished. A mixture of one volume of this gas with about ten volumes of air forms a most explosive mixture. It is called *Fire-Damp* by the miners. Such a mixture often occurs in coal mines, and when accidentally ignited brings death and destruction to numbers of our fellow-creatures. After explosion the fire-damp is converted into carbonic acid\* and water.

This brings me to the explanation of the principle of the *Safety Lamp*, the invention of Sir Humphry Davy. It is used for the purpose of giving light to coal miners in collieries where fire-damp occurs. In order that you may clearly understand the *principle on which its safety depends*, I must ask your attention to the following experiments:—

On this pencil I coil a piece of copper wire; having done so, I light this piece of wax candle. Observe now, when I put the spiral over the wick, that the candle 'goes out,' *i.e.* the flame is extinguished. Why is this? It is because a certain amount of heat is necessary for the continuance of the combustion of the candle, and after it is once lighted, the amount of heat required is evolved by the combination of the carbon, &c., in the candle with the oxygen in the air. Now metals being

\* Called *choke-damp* by the miners.

*good conductors* of heat, the copper wire conducts away some of the evolved heat, and thus *reduces the temperature below the point at which combination is possible*. This is the reason why the candle goes out. If now I heat the wire to redness, and then place it over the wick, it will not extinguish the flame. This shows plainly that it is the *chilling* effect of the cold metal which extinguishes the flame.

For the same reason the flame of a spirit-lamp or of a gas jet cannot pass through a screen of wire gauze. Observe, when I place this piece of wire gauze over the flame of a spirit-lamp, that the flame appears as if the top were cut off, the metallic wire conducts away a portion of the heat evolved during the combination of the vapour of the spirit with the oxygen of the air, and thereby reduces the temperature below the point at which combination is possible. If I apply a light to the vapour which passes through the meshes of the gauze, it will take fire and burn above as well as below. The same will happen if I redden the wire screen before applying it to the flame; hence, you perceive, it must be the chilling influence of the cold metallic screen that extinguishes the upper portion of the flame. I may even blow out the flame beneath the screen, and allow it to burn only above it.

You will now understand why a miner may enter an atmosphere of fire-damp with a Davy's Safety Lamp (Fig. 4) in his hand.

The lamp is a common oil lamp surrounded with a cylinder of wire gauze; the upper portion of the cylinder is usually double for the purpose of making it more secure.

When the miner meets with an atmosphere of fire-damp, the mixture enters the lamp and burns away inside, but, in consequence of the metallic



Fig. 4.

gauze intervening, the combustion cannot be propagated to the explosive gas outside the wire screen.

The miner knows, by the appearance of a *blue flame* in the interior of the lamp, when he is in contact with the fire-damp, and is thus cautioned to leave the mine till it is better ventilated.

We have seen that dry nitrate of copper refused to combine with tin-foil till it (the nitrate of copper) was dissolved by the addition of a few drops of water.\* Some metallic salts when strongly heated in a tube are decomposed, leaving the metal in a *fine state of division*, which, when shaken out into the air, immediately takes fire, owing to its combination with oxygen. Tartrate of lead thus treated forms the well-known lead pyrophorous. Hence we conclude that another condition favourable to the combination of two or more bodies consists in their being presented to each other in a *suitable molecular state*. Thus, some substances that readily combine when in the state of vapour will not do so at all when in the solid condition; for instance, if a piece of charcoal and a stick of sulphur be brought together, no chemical action takes place, whereas if the vapour of sulphur be brought into contact with red-hot charcoal, combination takes place, and a very explosive liquid, called bi-sulphide of carbon, is produced.

There are other minor conditions which are sometimes necessary for determining the combination of bodies—these shall be noticed as they occur in our course of study.

As a matter of fact, every new compound said to be made by the hand of the chemist is but the result of the fundamental laws of composition; the chemist simply provides conditions favourable for combination.

\* The particles of dissimilar solid bodies are brought into closer proximity by solution than when left in their original dry state. Hence *solution* generally favours *chemical action*, which takes place only at insensible distances.

## CHAPTER V.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

We shall now proceed to consider the laws which govern *the proportions by weight*, in which substances enter into chemical combination.

Here is some infusion of purple cabbage.\* I shall divide it into two portions, which I shall call *a* and *b*; now to the portion *a* I add a little soda; you observe that it becomes green; to the portion *b* I add a few drops of oil of vitriol (hydrogen sulphate), this you see turns it red; now I shall carefully add this red solution to the green one, drop by drop. You will observe that when *a certain quantity* of the red, or acid, solution has been added to the green, or alkaline, solution, the mixture will be restored to its original purple colour. If now I add another drop of the red, or acid, solution, the red colour will be again produced; if instead of adding an additional drop of the red solution to the mixture, I were to add a drop of the green, or alkaline, solution, the green colour would be immediately reproduced.

This experiment teaches us that the red and green solutions must be mixed together in a certain *fixed and definite proportion* in order to restore the original purple colour. The red solution contains sulphuric acid and the green soda, and when mixed together in some fixed and definite proportion, the purple colour is restored to the mixture, because, then the acid and alkaline constituents neutralize each other, in combining together to

\* In the absence of purple cabbage, tincture of litmus will answer the purposes required, but the changes of colour are not so striking as with the former. Tincture of violets may also be used for this experiment.



produce the definite compound sodium sulphate (sulphate of soda), which has neither acid nor basic action on the infusion of purple cabbage.\*

Common salt, when analysed, is always found to be composed of two elements, united together in *certain invariable proportions*, namely, 23 parts by weight of sodium and  $35\frac{1}{2}$  parts by weight of chlorine.

Water is always composed of two elements (hydrogen and oxygen), in the proportion of 2 parts by weight of hydrogen to 16 parts by weight of oxygen.

All known chemical compounds are found to consist of certain elements combined together in *invariable proportions*. In fact, a chemical compound is distinguished from a *mechanical mixture* by its being, *under all conditions*, composed of certain elements united *in fixed proportions by weight*, as well as by its possessing properties different from those of its proximate constituents.

Hence we deduce the first law of combination—

*The same chemical compound invariably consists of the same elements associated in a constant proportion.*

The question may now be asked—Can more compounds than one be formed out of the same elements? Yes, we know of five distinct compounds of the elements oxygen and nitrogen alone; they are:—

	<i>Parts by weight.</i>	<i>Parts by weight.</i>
1. Nitrogen Monoxide, containing 28 of Nitrogen	to 16 of Oxygen.	
2. Nitrogen Dioxide	28 " " "	32 " "
3. Nitrogen Trioxide	28 " " "	48 " "
4. Nitrogen Tetroxide	28 " " "	64 " "
5. Nitrogen Pentoxide	28 " " "	80 " "

You will observe that while the same quantity of nitrogen is found in each of these compounds, the quantity of oxygen is in the exact proportion of the numbers 1, 2, 3, 4, 5.

\* Compare page 91.

This is one of the most remarkable examples of the second law of combination, or the law of combination in multiple proportions. This law is expressed as follows:—

*When one body combines with several progressively-increasing proportions of another, giving rise to a series of distinct compounds, the higher proportions are simple multiples of the first, or lowest.\**

In every well-defined series of compounds this law obtains.

In the above example each proportion of the variable element (oxygen) is a multiple of the first, or lowest. Hence if any body can combine with more than 16 parts by weight of oxygen, it must combine with some other quantity of it which is a multiple of 16.† Analysis shows that all chemical compounds which contain sulphur yield either 32 proportions of it, or some multiple of that number. So also with the other elements; iron, for instance, is found always in the proportion of 56 parts by weight, or some multiple of that number.

Dalton, who discovered this law of multiple proportions, in endeavouring to explain why the elements combine in multiples of their combining proportions, propounded his celebrated *Atomic Theory*.

‘Reviving the idea of Leucippus and the expression of Epicurus, he supposed that bodies are formed of small individual particles, which he called *atoms*. To this old and vague notion he attached an exact meaning by supposing, on the one hand, that the atoms of each kind of matter possess a *constant weight*, and, on the other,

\* In some cases the proportion in which the elements unite is rather less simple, 2 proportions of one element combining with 3, 5, or 7 of the other.—*Miller*.

† Sixteen is the smallest proportion in which oxygen is known to enter into combination, and is therefore called its *combining proportion* or *atomic weight*.

that combination between two kinds of matter takes place, not by penetration of their substance, but by *juxtaposition of their atoms*. This fundamental hypothesis being admitted, the fact of definite proportions and the fact of multiple proportions are simply and satisfactorily explained. The *definite proportions* in which bodies combine represent the *constant ratios* between the weights of the juxtaposed atoms. *Multiple proportions* indicate the *variable numbers of atoms* of the same kind, which may unite with one or several atoms of another kind, this latter case being that in which several compounds are formed by the union of the same two bodies.\*

As the elements combine in fixed proportions by weight, if the smallest of these proportions be determined, we can represent them by numbers, and thus construct a table of numbers which will represent the combining weights of the elements. Such a table I will now show you. (See Table D.) These numbers, representing the combining proportions of the elements, are called their *atomic weights*, in accordance with Dalton's Theory, inasmuch as they represent the weights of their atoms, not the *absolute*, but the *relative*, weights.

'They are numbers expressing relations of weight. The term of comparison is the weight of one of the atoms taken as unity. Dalton chose hydrogen for the unit. These atomic weights of Dalton were called *equivalents* by Wollaston, *proportional numbers* by Davy; and we see that these notions of atomic weights and equivalents, which have since been separated, were originally confounded together, and represented nothing but the proportions by weight in which bodies combine.†

You are now prepared to receive the following table of atomic weights :—

\* History of Chemical Theory, by Ad. Wurtz.

† *Id.*

TABLE D,

*Showing the names, symbols and atomic weights of the more commonly occurring Elements.*

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminum....	Al	27.1	Mercury.....	Hg	200
Antimony ....	Sb	122	Molybdenum..	Mo	96
Arsenic .....	As	75	Nickel .....	Ni	59
Barium .....	Ba	137	Nitrogen ....	N	14
Bismuth ....	Bi	210	Oxygen .....	O	16
Boron.....	B	11	Palladium....	Pd	106.5
Bromine ....	Br	80	Phosphorus ..	P	31
Cadmium ....	Cd	112	Platinum ....	Pt	197
Calcium.....	Ca	40	Potassium....	K	39
Carbon .....	C	12	Selenium ....	Se	79.5
Chlorine.....	Cl	35.5	Silicon .....	Si	28
Chromium....	Cr	52.5	Silver .....	Ag	108
Cobalt.....	Co	59	Sodium .....	Na	23
Copper .....	Cu	63.5	Strontium....	Sr	87.5
Fluorine ....	F	19	Sulphur.....	S	32
Glucinum ....	G	9	Tellurium ....	Te	128
Gold .....	Au	197	Tin .....	Sn	118
Hydrogen ....	H	1	Titanium ....	Ti	50
Iodine.....	I	127	Tungsten		
Iron .....	Fe	56	(Wolfram)..	W	184
Lead .....	Pb	207	Uranium ....	U	240
Lithium.....	Li	7	Vanadium....	V	51
Magnesium ..	Mg	24	Zinc .....	Zn	65
Manganese....	Mn	55			

When we say that the atomic weight of oxygen is 16, what do we mean? Is it that an atom of oxygen weighs 16lbs., ozs., kilograms, grams, or such like? No, we mean nothing more than that an atom of oxygen is 16 times as heavy as an atom of hydrogen. Hydrogen being the lightest substance known, the weight of its atom is taken as *the unit by which the weights of the atoms of all other elements are measured.* Each atom of

any one element has the same weight as any other atom of the same element, under *all* circumstances. Each atom of any one element has the same volume, or bulk, as each atom of every other element, when under the *same* circumstances. This is equivalent to saying that the atoms of all the elements have the same size.\*

It may be asked, what quantity of any element are we to select in determining its atomic weight?

This question is answered by the following definition:—

‘The smallest quantity of any particular element, whether or not of itself volatile, that is found to exist in *two gaseous volumes* of any of its compounds, is taken as its atomic weight.’—(Odling).

The atomic theory being a subject of great difficulty to beginners in Chemistry, I have dwelt upon it at unusual length. I shall now turn your attention to the remaining laws of combination. The third law of combination may be stated as follows:—

*If two bodies combine in certain proportions with a third, they combine in the very same proportions with each other,† provided that combination between them be possible.*

Thus 16 parts of oxygen combine with 56 parts of iron, and 32 parts of sulphur combine with 56 of iron. This law simply states, that if it be possible for sulphur and oxygen to combine together, they will do so in the proportion of 32 parts sulphur to 16 oxygen, or in some simple multiple of those numbers.

This law has been verified by a number of exact analyses of compound bodies.

It has been proved by numerous experiments that the

\* The ‘law of volumes’ will be found more fully explained in Chapter VII.

† This, which is called the law of Reciprocal Proportion, is subject to the same variation as the Law of Multiples.

number representing the combining, or molecular, weight of a compound body is equal to the sum of the numbers representing the combining proportions of the elements which compose it. This experimental truth is set down by some chemists as a fourth law of combination, and is called the law of Compound Proportion.

Water, for example, always consists of 2 parts by weight of hydrogen and 16 of oxygen. The sum of these numbers 18 ( $=2 + 16$ ), is the number which invariably represents the combining proportion of water.

It appears a self-evident fact that the weight of a compound body should equal the sum of the weights of its components.

The laws of combination may be repeated here by way of recapitulation :—

I.—The law of constant (or definite) proportion.

*The same chemical compound invariably consists of the same elements associated in a constant proportion.*

II.—The law of multiple proportion.

*When one body combines with several progressively increasing proportions of another, giving rise to a series of distinct compounds, the higher proportions are simple multiples of the first, or lowest.*

III.—The law of reciprocal proportion.

*If two bodies combine in certain proportions with a third, they combine in the very same proportions with each other, provided that combination between them be possible.*

IV.—The law of compound proportion.

*The combining proportion of a compound body is equal to the sum of the combining proportions of its components.*

The first three laws are found to hold good for compounds which enter into combination (as a whole) without undergoing decomposition, as indeed might be inferred from the fourth law. Such compound groups are known as compound radicles.

An important help, in determining the atomic weights of the elements, is derived from the following law, discovered by Dulong and Petit :—

*The product of the atomic weight and specific heat of any elementary substance is a constant quantity.* This product is termed *atomic heat*. Every element, then, has the same atomic heat (about 6·2).

From this law it follows that the same quantity of heat is required to raise a single combining proportion of each of the elementary bodies through the same range of temperature; thus it takes the same amount of heat to raise 24 parts by weight of magnesium, 23 of sodium, 108 of silver, or 39 of potassium, through the same range of temperature. This fact may be expressed by saying that the specific heat of the atomic weight of every one\* of the elements is the same.

The atomic weights of many of the metals, which do not form volatile compounds, have been determined by the aid of this wonderful law; those weights of the different metals which have approximately the same specific heat as 65 parts of zinc, 118 parts of tin, and 210 parts of bismuth,† being selected as their respective atomic weights.

Faraday has discovered the remarkable law that *the quantity of electricity which is required to decompose one*

\* A few apparent exceptions exist.

† As zinc, tin, and bismuth form volatile compounds, their atomic weights are determined by the more direct method of finding the weight of the smallest quantity existent in two gas-volumes of such compounds.

*molecule of water will decompose a molecule of chloride of tin, a molecule of chloride of silver, or a molecule of any electrolyte. It is a 'golden truth that, under every variety of circumstances, the decompositions of the voltaic current are as definite in their character as those chemical combinations which gave birth to the atomic theory. This law of electro-chemical decomposition ranks, in point of importance, with that of definite combining proportions in chemistry.'*\*

It is a well-established fact that the quantity of electricity required to decompose a molecule of an electrolyte, in the decomposing cell, is generated by the conversion of an atom of zinc, by oxidation, into a molecule of zinc oxide: from this Faraday has concluded that 'the quantity of electricity which, being naturally associated with the particles of matter, gives them their combining power, is able, when thrown into a current, to separate those particles from their state of combination; or, in other words, that the electricity which is evolved by the decomposition of, and that which decomposes, a certain quantity of matter are alike.'

I have mentioned these laws here, as they appear to me to throw considerable light on the doctrine of atoms.†

\* 'Faraday as a Discoverer,' by Tyndall.

† Notwithstanding the beauty of the atomic theory, it is quite possible to regard Chemistry from an independent standpoint. If, for example, we define Chemistry to be—the study of the composition and properties of radicles (be they simple or compound) and of their action and reaction on one another to produce new compounds different from themselves—we obtain a definition of the science which is independent both of the theory of the existence of atoms as well as of the possibility of some of the so-called elements proving, hereafter, to be compound bodies. (See Chap. IX.)



## CHAPTER VI.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

The next subjects for consideration are *Nomenclature* and *Notation*.

I do not intend to enter upon the history of these subjects, or to ~~shall~~ only explain to you the principle by which the names of compound bodies are constructed in the present day. The names of the elementary bodies have already been given—*vide* Tables A and D.

The principle is to give, as much as possible, to compound bodies names indicative of their chemical composition. Thus, a compound resulting from the combination of an element with oxygen is called an *oxide* of that element: for example, when iron and oxygen unite the compound is called *oxide of iron*, or *iron oxide*, or in Latin *ferri oxidum*; a compound of iron and chlorine is called *chloride of iron*, &c. If sulphur takes the place of chlorine, we have a *sulphide of iron*, or *iron sulphide*.

Water, being a compound of hydrogen and oxygen, is called *oxide of hydrogen*, or *hydric oxide*.

Compounds, formed by the elements uniting in several proportions, are distinguished from each other by the use of the Greek and Latin prefixes.

The use of such prefixes is well illustrated by the names of the oxides of nitrogen. They are named—

Nitrogen	Mon-oxide,	from the Greek	Monos,	signifying the one	} Oxide.*
"	Di-oxide	"	"	Dis	
"	Tri-oxide	"	"	Treis	
"	Tetr-oxide	"	"	Tetra	
"	Pent-oxide	"	"	Pente	
				"	" two
				"	" three
				"	" four
				"	" five

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\*  $N_2O$ ,  $N_2O_2$ ,  $N_2O_3$ ,  $N_2O_4$ ,  $N_2O_5$ .

The Latin numerals are also, sometimes, employed: for example, a well-known compound, a molecule of which consists of one atom of manganese and two atoms of oxygen, is often called *bin-oxide* of manganese (from the Latin *bis* twice); it is also called the *deut-oxide*, signifying the second oxide, and the *per-oxide* (from the Latin particle *per*), signifying higher oxide of manganese. The lower oxides are usually termed *protoxides*, and the salts derived therefrom are known as *proto-salts*, in contradistinction to the *per-salts*, which are derivable from *per-oxides*.

The terminations '*ous*' and '*ic*' have now come into general use; the latter is applied to a compound, which contains a greater proportion of any elementary or compound group than the compound (of the same elements) to which the termination '*ous*' is applied. This will be better understood by a few examples. Thus, the protoxide, or mon-oxide of *iron*, containing one atom of iron and one atom of oxygen (in every molecule), is called *Ferrous Oxide*, while another oxide, the *per-oxide*, containing two atoms of iron and three of oxygen (in every molecule), is called *Ferric Oxide*. The proto-sulphate of iron, too, is generally called *Ferrous Sulphate*, and the persulphate of iron is known as *Ferric Sulphate*.

The names of many salts which are formed from acids whose names end in '*ic*' are made to terminate in '*ate*,' and those which are formed from acids whose names end in '*ous*' are made to terminate in '*ite*.' For example, salts of sulphurous acid are called *Sulphites*, while those derived from sulphuric acid are called *Sulphates*.

We frequently indicate compounds, by writing down their chemical composition, by means of the symbols of the elements of which they are composed,—thus the inconveniences arising from the use of the long compound

names of the present nomenclature are, in a great measure, removed by what we call *Notation*, or the representation of the substances indicated by their respective names by *symbolical expressions*. Thus the symbol for oxygen, O, represents not oxygen in the general sense, but 16 parts by weight of oxygen; so also Fe signifies not iron merely, but 56 parts by weight of iron, and when the symbols Fe and O are placed together, thus, FeO, they represent the compound body formed by the combination of one atom of iron with one atom of oxygen, *i.e.*, a molecule of oxide of iron, or ferrous oxide, whose combining (or molecular) weight is  $72 = (56 + 16)$ .

FeO is called the *formula* of ferrous oxide: in a similar manner a molecule of the per-oxide of iron, or ferric oxide, is represented by the formula  $\text{Fe}_2\text{O}_3$ ; in this case the compound is composed of 2 atoms of iron and 3 atoms of oxygen, and the number of atoms of each element composing it is indicated by a small figure, placed to the right hand of its symbol and a little below it. It may also be written thus,  $\text{Fe}^2\text{O}^3$ , by placing the figures above; the former, however, is the most usual method, and will be adopted at these lectures.

When we want to express two molecules of any compound, we do so by writing the co-efficient 2 before the formula for one molecule; thus  $2\text{FeO}$  represents two molecules of ferrous oxide ( $= 2$  atoms of iron and 2 atoms of oxygen), and  $2\text{Fe}_2\text{O}_3$  indicates two molecules of ferric oxide; the co-efficient 2, in each case, multiplies all that comes after it. Hence in two molecules of ferric oxide, there are 4 atoms of iron and 6 atoms of oxygen; three molecules are expressed in a similar manner, by prefixing the figure 3, thus  $3\text{Fe}_2\text{O}_3$ ; any number of molecules  $n$ , are expressed thus,  $n \text{Fe}_2\text{O}_3$ .

Compound bodies are usually divided into classes, or orders, thus :—

1. *Binary* compounds are those which consist of only two elements.

*Examples.*

Name.	Formula.
Sodium Chloride (common salt).....	NaCl
Hydric Oxide (water) .....	H <sub>2</sub> O
Ferrous Oxide .....	FeO
Ferric Oxide .....	Fe <sub>2</sub> O <sub>3</sub>
Carbonic Anhydride (choke-damp) .....	CO <sub>2</sub>

2. *Ternary* compounds are those which consist of only three elements.

*Examples.*

Name.	Formula.
Calcium Carbonate.....	Ca CO <sub>3</sub> , or CaO, CO <sub>2</sub>
Potassium Nitrate (nitre) ...	KNO <sub>3</sub>
Ferrous Hydrate .....	FeH <sub>2</sub> O <sub>2</sub> , or FeO, H <sub>2</sub> O
Ferric Hydrate .....	Fe <sub>2</sub> H <sub>6</sub> O <sub>6</sub> , or Fe <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O
&c.	&c.

3. *Quarterternary* compounds are those which contain only four elements.

*Example.*

Name.	Formula.
Burnt Alum .....	KAl (SO <sub>4</sub> ) <sub>2</sub> = K + Al + S <sub>2</sub> + O <sub>8</sub>

There are compounds containing a greater number, and each is classed according to the number of elements it contains: a compound containing *five elements* would be called *quinary*, and so on. As an example of a quinary compound, I may mention crystallized alum:—



It is much to be regretted that a uniform system of naming chemical compounds has not yet been universally adopted. The fact that the same thing is frequently called by different names is often the cause of the dislike which boys take to the study of scientific names in general. It is, indeed, confusing to be told that the formula  $\text{H}_2\text{SO}_4$  stands for the well-known substance *oil of vitriol*, when this liquid is variously spoken of by chemists as sulphuric acid, hydrogen sulphate, hydric sulphate, dihydric sulphate, &c.; again, the familiar gas known to miners as *choke-damp* is likewise variously termed carbonic acid, carbon-dioxide and carbonic anhydride. In the absence, then, of an uniform system of nomenclature, I purpose, in these lectures, to employ familiar and popular names in common with the systematic ones employed by theoretical chemists; and in justification of this plan I quote the following words from the preface to Dr. Odling's work on chemistry (1870):—‘The preference habitually accorded by different chemists to trivial or to systematic names for general use is largely a matter of individual liking. For myself, I like, where they are sufficient for the purpose, to employ such trivial names as nitre, alum, potash, borax, green vitriol, bleaching powder, sal-ammoniac, muriatic acid, prussic acid, alcohol, wood spirit, marsh-gas, chloroform, acetic ether, phosgene, &c., &c., alternatively with the systematic names for the respective compounds.’

## CHAPTER VII.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

We now arrive at a subject of great importance, *viz.* the *Law of Volumes*, also called the *Law of Combination by Volume*, to the explanation of which I shall now proceed.

This law may be stated thus :—

*The atomic volumes of all elementary bodies,\* when measured in the gaseous state, and under the same conditions of temperature and pressure, are the same.* This is equivalent to saying that the spaces occupied by the quantities of the elements represented by their atomic, or combining, weights are equal when measured in the gaseous states, and under equal conditions of temperature and pressure. Thus the volume, or bulk, of 1 gram of hydrogen at the temperature  $0^{\circ}$  C. and pressure 760 m.m. (= height of the mercury in the barometric column) always measures 11.2 liters.† Again, if we take 16 grams of oxygen, and measure its bulk when its temperature is reduced to  $0^{\circ}$  C. and when the mercury in the barometric column stands at a height of 760 m.m., we shall find that the space it occupies is represented by 11.2 liters. Under the same conditions, the volume occupied by  $35\frac{1}{2}$  grams of chlorine or by 14 grams of nitrogen is 11.2 liters (=11200 cubic centimeters).

Hence it is plain that if the numbers representing the atomic weights of the elementary gases be taken in grams,

\* Phosphorus and arsenic, also zinc, cadmium and mercury form exceptions to this otherwise general law. (See page 61.)

† The volume of 1 gram of hydrogen, at  $0^{\circ}$  C. and 760 m.m. pressure is called *one gas-volume*.

and the volumes occupied by these weights measured at 0° C. and 760 m.m. pressure, they will each be found to occupy a bulk of 11·2 liters.

Therefore the *atomic*, or *combining*, *volumes* of the gases hydrogen, oxygen, nitrogen and chlorine are the same, and each of them is represented by 11·2 liters, or *one gas-volume*.

[*Note*.—0° C. and 760 m.m. are the *standards* of temperature and pressure at which the volumes of all gaseous bodies should be compared.]

On the other hand, the weights of 11·2 liters\* of hydrogen, oxygen, chlorine and nitrogen are 1, 16, 35½, and 14 grams respectively, *i.e.* the relative weights of equal volumes of these gases are represented by their combining proportions, or atomic weights; and as the *specific gravities of bodies are represented by the relative weights of equal bulks* (under the same conditions), it follows that the numbers, 1, 16, 35½ and 14 represent the specific gravities of hydrogen, oxygen, chlorine and nitrogen respectively.

We thus arrive at the important conclusion that the *same numbers represent both the atomic weights and specific gravities* of the elementary gases hydrogen, oxygen, chlorine and nitrogen.

What is true of these gaseous elements is also true of the other elements (with the five exceptions already mentioned) when in the gaseous condition.

For these reasons, as well as the fact that all elementary gases expand or contract equally for equal increments or decrements of temperature, and are similarly affected by similar changes of pressure, we are led to the conclusion that *equal volumes of the elementary bodies contain the same number of atoms*. This hypothesis

\* In all comparisons of gaseous volumes, the volumes are understood to be measured at the fixed standards, unless it be otherwise stated.

was first announced by Gerhardt, the originator of the modern unitary system of chemistry, which may be said to be based on the following three propositions :—

1. *That the atomic volumes of all the elements are the same (=one gas-volume).*
2. *That the molecular volumes of all compound bodies are the same (=two gas-volumes).*
3. *That although the combining volume of a compound be double that of an element, yet the ratio between the volumes of the smallest quantities, either of a compound or element, which can exist in a free (or uncombined) state, is one of equality.\**

We have already seen that the atomic volume of each of the elements (with five exceptions) is the same as that of hydrogen, or one gas-volume (=11.2 liters). Here, as in the case of atomic weights, the atomic volume of hydrogen is chosen as the *unit of reference*.

In chemistry we define the *specific gravity*, or *density*, of a body (whether an element or a compound) to be *the weight of one gas-volume*; in this case also, hydrogen, being the *lightest known substance*, is taken as the unit, and therefore the specific gravity of hydrogen (or weight of one gas-volume) = 1.

A great convenience, in calculation, arises from making *hydrogen the standard of comparison, or unit, to which all other bodies are referred*. Hence the specific gravity of hydrogen and its combining proportion, either by weight or by volume, are each represented by unity.

Sp. Gr.	At. Wt.	At. Vol.
---------	---------	----------

Thus hydrogen has ...1	1	1
------------------------	---	---

A knowledge of the law of combination by volume is

\* Because the smallest quantity of an element capable of existing by itself is regarded as a molecule, and occupies two gas-volumes.



of great importance to the practical chemist, inasmuch as it is easier to measure a given volume than a given weight of gas.

Hydrogen chloride ( $\text{HCl}$ ), commonly called hydrochloric acid, muriatic acid, or spirits of salts, is composed of 1 part by weight of hydrogen and  $35\frac{1}{2}$  parts by weight of chlorine, or, since the atomic proportions of the elements have equal volumes, it may be represented as composed of one volume of hydrogen and one volume of chlorine; and surely, you will allow that it is much easier to measure off a certain volume, as 11.2 liters, than to weigh out  $35\frac{1}{2}$  grams of chlorine gas.

One atom of oxygen combines with 2 atoms of hydrogen to form the well-known substance water ( $\text{H}_2\text{O}$ ), or, in consequence of each atom occupying the same volume, water may be represented as composed of 1 volume of oxygen and 2 volumes of hydrogen.

So also, a gaseous molecule of ammonia ( $\text{H}_3\text{N}$ ), being composed of 1 atom of nitrogen and 3 atoms of hydrogen, may be represented as composed of 1 volume of nitrogen and 3 volumes of hydrogen.

In each of these three cases, the volume of the resulting molecule produced by the combination of—

1 volume of hydrogen with 1 volume of chlorine

2 volumes        "        "        1        "        oxygen

3 volumes        "        "        1        "        nitrogen

is universally found by experiment to be exactly equal to twice the volume of 1 atom of hydrogen, and therefore equal to *two gas-volumes*.

Hence we see—

(1) That two volumes of hydrochloric acid are composed of 1 volume of hydrogen and 1 volume of chlorine, and in this case there is no condensation of volume.

(2) That two volumes of water-gas (steam) are com-

posed of 2 volumes of hydrogen and 1 volume of oxygen, and in this case there is a condensation of 3 volumes into 2.

- (3) That two volumes of ammonia are composed of 3 volumes of hydrogen and 1 volume of nitrogen, and hence in this case there is a condensation of 4 volumes into 2.\*

You are already aware that the specific gravity of an element is represented by the same number as its atomic weight. The question now arises—how are we to determine the specific gravity of a compound?

Recollect that whenever I use the term specific gravity, or density, without qualification, I mean the *chemical* specific gravity, or density—(i.e., Sp. Gr. with reference to hydrogen as the unit)—or the weight of one gas-volume. You will find, in books on Natural Philosophy, that the densities of bodies are referred to water as the unit, and sometimes to air, and, to avoid confusion, I must ask you to remember this distinction.

The specific gravity of hydrochloric acid has been experimentally determined and found to be  $18\frac{1}{2}$ ; that is, one gas volume of hydrogen chloride is  $18\cdot25$  times as heavy as the same bulk of hydrogen. Now a molecule of this compound consists of 1 part by weight of hydrogen and  $35\frac{1}{2}$  parts of chlorine, and its molecular weight is  $1 + 35\frac{1}{2} = 36\frac{1}{2}$ , and as  $18\frac{1}{2}$  is exactly half of  $36\frac{1}{2}$ , it is clear that the specific gravity of hydrogen chloride = *half its molecular weight*.

The specific gravity of steam is found to be 9, that is, one gas-volume of steam weighs 9 times as much as the same bulk of hydrogen. Water is composed of 2 parts by weight of hydrogen and 16 parts by weight of oxygen;

\* Condensation of volume affords evidence of chemical action having taken place. In all cases the volume after combination is always 2. Gay-Lussac was the first to notice this law.

therefore its molecular weight is  $2 + 16 = 18$ , which is exactly twice 9; hence the density of steam = *half its molecular weight*.

The density, or weight, of one gas-volume of ammonia has been found experimentally to be  $8\frac{1}{2}$ , and since ammonia consists of 3 parts by weight of hydrogen and 1 part of nitrogen, its molecular weight must be  $3 + 14 = 17$ . Therefore, in this case also, the specific gravity = *half the molecular weight*.

The *unit of molecular volume* adopted by chemists being the space occupied by 2 gas-volumes, the *unit of molecular weight* is therefore the weight of 2 gas-volumes. Hence, since we have defined the specific gravity of a body to be (chemically speaking) the weight of one gas-volume, it follows that *the specific gravity of any body = half its molecular weight*.

As the equality in volume of all gaseous molecules, irrespective of the number of atomic volumes which enter into their composition, is a well-established law, it follows (for the same reasons that equal volumes of the elements contain the same number of atoms) that *equal volumes of compound gases contain the same number of molecules*—not atoms, for the molecules of some compound gases contain more atoms than others; thus the ammonia molecule we have seen contains four atoms, while the water molecule contains but three, and hydrochloric acid molecule only two atoms. We are thus led inductively to the general statement known as Avogadro's law—that *equal volumes of all substances, when in a state of gas, and under like conditions of temperature and pressure, contain the same number of molecules*—which is but a more general statement of this principle.\*

\* This law of Avogadro is the basis of the molecular theory.

The smallest bulk of matter that can exist by itself in a separate state being a molecule, it follows that when hydrogen—or any other elementary body—occurs in a *free* state, it may be represented by a formula which indicates both its molecular weight and volume, thus:—

$$\text{H}_2 = (2 \text{ parts by weight}) = (2 \text{ volumes}).$$

The following table exhibits the relations between the specific gravities and molecular weights of simple and compound bodies:—

TABLE E,

*Showing the relations between specific gravities and molecular weights of simple and compound bodies.*

Sp. Gr. = Wt. of 1 Gas-Vol.		Molecular Wt. = Wt. of 2 Gas-Vols.	
Simple Bodies.	H = 1	H <sub>2</sub> = 2	}
	O = 16	O <sub>2</sub> = 32	
	N = 14	N <sub>2</sub> = 28	
	Cl = 35.5	Cl <sub>2</sub> = 71	
Compound Bodies.	HCl	HCl = 36.5	}
	$\frac{\text{H}_2\text{O}}{2} = 18.25$	H <sub>2</sub> O = 18	
	$\frac{\text{H}_2\text{O}}{2} = 9$		
	$\frac{\text{H}_3\text{N}}{2} = 8.5$	H <sub>3</sub> N = 17	

With but few exceptions the molecules of all bodies occupy the same volume, and this fact is made considerable use of, as an aid to the chemist, in determining the molecular formulæ of compounds; thus the formulæ Fe<sub>2</sub>Cl<sub>6</sub>, Cr<sub>2</sub>Cl<sub>6</sub> and Al<sub>2</sub>Cl<sub>6</sub> are given to ferric chloride, chromic chloride, and aluminic chloride, respectively, instead of the formulæ FeCl<sub>3</sub>, CrCl<sub>3</sub> and AlCl<sub>3</sub>, which have evidently the

same ratio of constituent atoms,—for this reason, that the former formulæ correspond to two gas-volume molecules, while the latter represent only single volume molecules, and are therefore inconsistent with our theory.

The chemical specific gravities, or *vapour-densities*, of volatile compounds are most valuable as a means of determining the atomic weights of the elements. As an example: let it be proposed to determine the atomic weight of mercury. Now, mercury combines with chlorine to form volatile compounds, one of which is called *mercuric chloride*, the vapour-density or weight of one gas-volume of which is found to be  $135\frac{1}{2}$ . It is further found, by analysis, to contain in *one volume*  $35\frac{1}{2}$  parts by weight of chlorine and 100 parts by weight of mercury. Why, then, is not the atomic weight of mercury 100, as that of chlorine is  $35\frac{1}{2}$ ? Because the atomic weight (as already defined) is the weight of the smallest quantity contained in *two volumes*. Consequently, since one volume of mercuric chloride contains 100 parts of mercury and  $35\frac{1}{2}$  of chlorine, two volumes, or one molecule, must contain 200 parts of mercury and 71 parts of chlorine. It is hence concluded that the smallest quantity of mercury contained in two gas-volumes of mercuric chloride is 200 parts, and therefore, that the atomic weight of mercury is 200; and since  $71 = \text{twice } 35\frac{1}{2}$ , the known atomic weight of chlorine, a molecule of mercuric chloride may be represented by the formula  $\text{HgCl}_2$ . There is another chloride of mercury called calomel, or *mercurous chloride*, the formula of which is  $\text{Hg}_2\text{Cl}_2$ .

That 200 is the atomic weight of mercury is confirmed by the law of Dulong and Petit, which states that the atomic weight multiplied by the specific heat of each of the elements is a constant quantity. This quantity, which is called the atomic heat, is represented (as you already know) by 6.2. Now, the specific heat of mercury

being  $\cdot 032$ , if 200 be its atomic weight, then its atomic heat  $= 200 \times \cdot 032 = 6\cdot 4$ , which is very nearly the same as the *mean value*  $6\cdot 2$ ; whereas if 100 be taken as the atomic weight of mercury, its atomic heat will be only  $3\cdot 2$ , or almost exactly half that of the other metallic elements; and as such a result is forbidden by Dulong and Petit's beautiful law, 200 must be adopted as the atomic weight of mercury.

The problem that we have just solved affords as good an illustration as you could have of the practical application of vapour-densities, as well as of the use of the law of atomic heat.

When speaking of gaseous volumes, you may remember that phosphorus, arsenic, zinc, cadmium and mercury were mentioned as exceptions to the general law of combination by volume, which states that the atomic volumes of all the elements are the same.

If you refer to the Table of Atomic Weights (Table D, page 43), you will find that the atomic weights of these bodies are there given as in the second column of the following Table :—

TABLE F,

*Showing the relations between the Atomic Weights, Vapour-Densities and Atomic Volumes of Phosphorus and Arsenic—and of Zinc, Cadmium and Mercury.*

Name.	Atomic Weight (H=1)	Vapour-Density. (H=1)	Mol. Wt. (H <sub>2</sub> =2)	Number of atoms in the Molecule.
{ Phosphorus ..	31	62	124	4
{ Arsenic .....	75	150	300	4
{ Zinc .....	65	32·5	65	1
{ Cadmium ....	112	56	112	1
{ Mercury ....	200	100	200	1

These five elements form exceptions\* to the 'law of volumes,' inasmuch as their atomic weights differ from their specific gravities.

The relations between the atomic weights, vapour-densities and atomic volumes of the five elements in question is exhibited in Table F. Phosphorus and arsenic have vapour-densities which are exactly double their atomic weights; while, on the other hand, the vapour-densities of zinc, cadmium and mercury are exactly half their atomic weights.

Again, the atomic volumes of phosphorus and arsenic are each equal to one-half that of hydrogen, whereas the atomic volumes of the other three elements—zinc, cadmium and mercury—are equal to twice that of hydrogen, or two gas volumes. The phosphorus and arsenic molecules, therefore, contain 4 atoms each, while the molecule of each of the other three elements contains but 1 atom.

These anomalous results would be removed if we were to double the atomic weights of phosphorus and arsenic, and at the same time to halve those of zinc, cadmium and mercury.

You will probably say, Why not do so, and thus make the law of gaseous volumes a universal truth? We do not do so—

1st—Because, if it were done, the atomic heat of these elements would not then be the same as those of the other elements, which is the case when the present atomic weights are adopted.

2ndly—Because, with their present atomic weights a molecule of the volatile compounds of these elements occupies two gas-volumes, but if their atomic weights be altered, as suggested, a molecule of their gaseous

\* The molecule of sulphur contains 6 atoms, but sulphur is most probably a compound body. (See footnote p. 64.)

compounds would not then correspond with the established law of the *equality of all molecular volumes*,—e.g. if the atomic weights of phosphorus and arsenic be doubled, then the molecular bulk of each would be equal to 4 gas-volumes—the molecular bulk being the volume of a molecule, the weight of which is twice the vapour-density.

You will thus perceive that we cannot alter the atomic weights of the elements without infringing two already well-established and important laws, so that you must be satisfied to adopt, as proper atomic weights, the numbers given in Table D, which are founded on experimental facts, and are in harmony with the law of volumes, Avogadro's law, the law of Dulong and Petit, and the doctrine of isomorphism.

Since the vapour-density of a body =  $\frac{1}{2}$  its molecular weight, the *theoretical* density, or specific gravity,\* of any gaseous compound may be deduced from its molecular formula, thus—

Let it be required to find the density (or specific gravity) of iodide of hydrogen, otherwise called hydriodic acid. The molecular formula of hydriodic acid is HI. On referring to Table D (p. 43) we find the atomic weights of hydrogen and iodine to be 1 and 127 respectively: therefore the molecular weight of iodide of hydrogen ( $HI=1+127$ )=128; but density= $\frac{1}{2}$  molecular weight: therefore the density of hydriodic acid =  $\frac{128}{2} = 64$ , i.e. it is 64 times as heavy as hydrogen.

As another example:—Let it be required to determine the specific gravity of hydrogen sulphide. This is the stinking gas, commonly called sulphuretted hydrogen. Its molecular formula is  $H_2S$ . Now the atomic weight of

\* Specific gravities properly mean relative, or specific, weights.



sulphur is 32, therefore  $H_2S = 2 + 32 = 34$ . Hence the specific gravity of hydrogen sulphide  $= \frac{34}{2} = 17$ .

These examples are sufficient to illustrate the method of determining the theoretic specific gravities, or vapour-densities, of gaseous bodies.

In some books on chemistry you will find two vapour-densities given; the one called the Theoretical and the other the Experimental density; and in consequence partly of errors in the measuring and weighing of gases, and partly because the volumes may not have been measured at temperatures sufficiently removed from their points of condensation, the densities determined by experiment occasionally differ from those derived from theory.\*

Moreover, in the practical determinations of vapour-densities it often becomes necessary to raise the substance operated on to a *very high temperature* in order to bring it into the condition of a true gas; and thus it sometimes happens that the elements of a compound body become *dissociated*, or part company.†

I shall now describe to you a simple method of determining vapour-densities experimentally.

For this purpose a large globe, fitted with a stop-cock, and having a certain known capacity, is exhausted of air by means of an air-pump; it is then weighed while empty, after which it is screwed on to a transferring jar (Fig. 5), and filled with hydrogen gas; when this is done it is again weighed; the increase of weight gives the weight of the globe full of hydrogen. The globe is again

\* The sulphur molecule consists of the ordinary 2-atom molecule if the determination of its v. d. be made at a sufficiently high temperature, but of 6 atoms if its v. d. be taken near to its boiling point.

† Thus at very high temperatures even the elements of water may be separated by dissociation.

exhausted, and then filled with the gas whose density is to be determined, and again weighed; the difference between this weight and that of the empty globe gives the weight of the gas. If the weight thus found be divided by the weight of the globe full of hydrogen, the quotient will represent the specific weight (or gravity) of the gas compared to that of hydrogen.



Fig. 5.

In performing these experiments both the hydrogen and other gas should be passed through a drying tube before entering the globe; they should also be weighed under the same conditions of temperature and pressure, otherwise corrections for volumes will have to be introduced. The methods of applying such corrections I propose to explain in the next chapter. If the capacity of the globe were 11.2 liters, or one gas volume, at the temperature  $0^{\circ}\text{C.}$  and pressure 760 m.m. it would be found to contain, at that temperature and pressure, the following weights of the different elementary gases, when perfectly dry :

1	gram of H <sub>2</sub>	Hydrogen.
16	grams „	Oxygen
14	„ „	Nitrogen.
35.5	„ „	Chlorine.

The author considers it inadvisable to trouble the beginner at so early a stage with the elegant method of determining the specific gravities of vapours recently introduced by Messrs. Victor and Carl Meyer. He must refer to larger works for information on the subject when his progress in Chemistry warrants it. For the various methods of determining the specific gravities of solids and liquids, the student is referred to any standard work on hydrostatics.

## CHAPTER VIII.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

Now that we know the different weights of a certain fixed volume (11·2 liters) of the elementary gases, under the standard conditions of temperature and pressure, we can easily calculate the weights corresponding to any other volumes, or conversely, the volumes corresponding to any given weights of them, at the same standards. For example—Let it be required to calculate the weight of 20 liters of oxygen at 0° C. and 760 m.m. barometric pressure.

Since 11·2 liters weigh 16 grams—

1 liter must weigh  $\frac{16}{11\cdot2}$  grams.

Therefore 20 liters must weigh  $\frac{16}{11\cdot2} \times 20 = 28\cdot57$  grams.

Or the problem may be solved by simple proportion, as follows :—

$$\begin{array}{cccc} \text{liters} & & \text{liters} & \text{grams} & \text{grams} \\ 11\cdot2 & : & 20 & :: & 16 & : & x \end{array}$$

$$\text{Therefore } x = \frac{20 \times 16}{11\cdot2} = \frac{320}{11\cdot2} = 28\cdot57 \text{ grams.}$$

Let us now take, as examples of the converse operation, the following problems :—

*Problem.*—To find the volume, at the normal\* temperature and pressure of 50 grams of hydrogen ?

As 1 gram occupies 11·2 liters—

50 grams must occupy  $11\cdot2 \times 50 = 560$  liters.

*Problem.*—What is the volume of 48 grams of oxygen at the normal temperature and pressure ?

\* From *norma*, a rule,—0° C. and 760 m.m.

Since 16 grams occupy 11·2 liters—

1 gram must occupy  $\frac{11\cdot2}{16}$  liters ;

Therefore 48 grams occupy  $\frac{11\cdot2}{16} \times 48 = 33\cdot6$  liters.

Or by simple proportion thus—

$$\begin{array}{cccc} \text{grams} & \text{grams} & \text{liters} & \text{liters} \\ 16 & : 48 & :: 11\cdot2 & : x \end{array}$$

Therefore  $x = \frac{11\cdot2 \times 48}{16} = 33\cdot6$  liters.

The weight of 1 liter of hydrogen, at the standard temperature and pressure, ought to be remembered by every chemist ; it may be determined as follows :—

Since 11·2 liters weigh one gram,

1 liter must weigh  $\frac{1}{11\cdot2}$  gram.

When the fraction  $\frac{1}{11\cdot2}$  is turned into the decimal form it becomes ·0893 as nearly as possible.

Note, therefore, that *one liter of hydrogen weighs ·0893 of a gram, at 0° C. and 760 m.m.*

Dr. Hofmann adopts the weight of a liter of hydrogen, at the standard temperature and pressure, as the *unit of weight*, and from the *liter-weight* of hydrogen he calculates the weight of an equal volume of any other gas (under the same conditions).

He describes the use of the liter-weight of hydrogen as follows :—

So important, indeed, is this standard weight unit that some name, the simpler and briefer the better, is needed to denote it. For this purpose I venture to suggest the term *crith*, derived from the Greek word *κριθ* signifying a barley corn, and figuratively employed to imply a small weight. The weight of 1 liter of hydrogen being called 1 *crith*, the volume-weight of other gases, referred to hydrogen as a standard, may be expressed in terms of this unit.

'For example, the *relative volume-weight*\* of chlorine being 35·5, that of oxygen 16, that of nitrogen 14, the actual weight of 1 liter of each of these elementary gases, at 0° C. and 0·76 m. pressure, may be called respectively 35·5 *criths*, 16 *criths*, and 14 *criths*.

'So, again, with reference to compound gases, the *relative volume-weight* of each is equal to half the weight of its product volume.† Hydrochloric acid (HCl), for example, consists of 1 volume of hydrogen + 1 volume of chlorine = 2 volumes, or, by weight, 1 + 35·5 = 36·5 units; whence it follows that the relative volume-weight of hydrochloric acid gas is  $\frac{36\cdot5}{2} = 18\cdot25$  units, which last figure, therefore, expresses the number of *criths* which one liter of hydrochloric acid gas weighs at 0° C. temperature, and 0·76 m. pressure . . . . .

'So once more, as the product volume of water-gas (H<sub>2</sub>O) (taken at the above temperature and pressure) contains two volumes of hydrogen + 1 volume of oxygen, and therefore weighs 2 + 16 = 18 units, the single volume of water-gas weighs  $\frac{18}{2} = 9$  units, or, substituting as before the concrete for the abstract value, 1 liter of water-gas weighs 9 *criths* . . . . .

'And so, lastly, of ammonia (H<sub>3</sub>N): it contains in 2 liters 3 liters of hydrogen, weighing 3 *criths*, and 1 liter of nitrogen, weighing 14 *criths*; its total product-volume-weight is therefore 3 + 14 = 17 *criths*, and its single-volume or liter-weight, is consequently  $\frac{17}{2} = 8\cdot5$  *criths*. . .

'Thus by the aid of hydrogen-liter-weight, or *crith* employed as a common multiple, the actual, or concrete

\* Relative volume-weight = specific weight, or specific gravity.—S.C.

† Product-volume = Molecular volume.—S.C.

weight of 1 liter of any gas, simple or compound, at standard temperature and pressure, may be deduced from the mere abstract figure expressing its volume-weight *relatively* to hydrogen.\*

‘From this knowledge, the weight of one liter† of any gas, simple or compound, at *any other* than standard temperature or pressure, or under any variation both of standard temperature and pressure, may be deduced, by the application of the formulæ, devised by physicists to express the laws of expansion and contraction for gases under varying conditions of temperature and pressure.’

We are now prepared to discuss these laws, and from them to deduce the formulæ referred to by Dr. Hofmann. For this purpose I must ask you to take the following *Experimental Laws* for granted, without being actually proved to you. They rest on the authority of many eminent experimenters, such as Dalton, Gay-Lussac, Regnault, Boyle, Marriotte, &c., and can be easily verified by direct experiment. Their demonstration belongs more to the province of Physics than to that of Chemistry.

*I.—All gases expand and contract alike, for equal increments and decrements of temperature.*

*II.—For every increment of 1° C. in temperature, a gas expands  $\frac{1}{273}$  ( $=\cdot003665\frac{1}{3}$ ) of its original volume at 0° C.*

\*The actual weight in grams of one liter of any gas is, therefore, obtained by multiplying its number of criths by the common multiple  $\cdot0893$ , which we have already found to be the weight of 1 liter of hydrogen, at the standard temperature and pressure: *e.g.*, the weight of 1 liter of oxygen, containing 16 criths, is  $16 \times \cdot0893 = 1\cdot429$  grams.—S.C.

† And consequently, by multiplication, of any number of liters.

‡ The vulgar fraction  $\frac{1}{273}$  or the decimal fraction  $\cdot003665$  is called the coefficient of expansion (per degree) of gases.

From this (Gay-Lussac's law) it follows that 1 volume of gas at  $0^{\circ}$  C. becomes 1.003665 volumes at  $1^{\circ}$  C.,  $(1 + .003665 \times 2)$  volumes at  $2^{\circ}$  C. and  $(1 + .003665 \times t)$  volumes at  $t^{\circ}$  C.

Also 273 volumes at  $0^{\circ}$  C.  
 become 274 „ „  $1^{\circ}$  C.  
 „ 275 „ „  $2^{\circ}$  C.  
 and  $(273 + t)$  „ „  $t^{\circ}$  C.

It is therefore evident that the volume of a gas may be doubled by raising its temperature from  $0^{\circ}$  C. to  $273^{\circ}$  C.

If, now, it be required to ascertain what volume would be occupied by a certain quantity of gas whose volume at  $0^{\circ}$  C. was 100 (cubic centimeters, cubic inches, or cubic anythings), when its temperature is *raised* to (let us say)  $15^{\circ}$  C?

The calculation is made as follows:—

Its volume at  $0^{\circ}$  C. is to its volume at  $15^{\circ}$  C. (according to *Law II.*) in the ratio of 273 to  $(273 + 15)$ ; therefore if its volume at  $15^{\circ}$  C. be  $x$ ,  $x$  may be found from the proportion

$$273 : (273 + 15) :: 100 : x$$

$$\text{Therefore } x = \frac{273 \times 100}{288} = 105.49.$$

Conversely, if we wish to know what volume 100 (cubic centimeters, inches, &c.) measured off at  $15^{\circ}$  C., will occupy when its temperature is *reduced* to  $0^{\circ}$  C.?

We proceed thus:—

Since gases contract (according to *Law I.*) for a given *decrease* of temperature, by the same amount as they expand for a corresponding *increase* of temperature, its volume at  $15^{\circ}$  C. is to its volume at  $0^{\circ}$  C. as  $(273 + 15)$  is to 273; therefore calling  $x$  its volume at  $0^{\circ}$  C.,  $x$  may be found from the proportion.

$$(273 + 15) : 273 :: 100 : x$$

$$\text{Therefore } x = \frac{273 \times 100}{288} = 94.8 \text{ nearly.}$$

The processes of calculation adopted in these two examples may be otherwise stated, by the following formulæ, in which  $\cdot 003665$  is used, instead of the vulgar fraction  $\frac{1}{273}$ , for the coefficient of expansion of gases per degree.

$$V_t = V_0 (1 + \cdot 003665 t) \dots \dots \dots [1]$$

This formula, in which  $V_0$  is the volume at the temperature  $0^\circ$  C., and  $V_t$  the volume corresponding to any temperature  $t^\circ$  (above zero), is suited to calculations similar to that given in the first example. Mere inspection of this formula will satisfy you that it is only a *general statement* of the principle adopted in the first calculation, which I shall now repeat as an illustration of the use of the formula; making the necessary substitutions, we may write our formula thus:—

$$\begin{aligned} V_{15} &= V_0 (1 + \cdot 003665 \times 15) \\ &= 100 (1 + \cdot 054975) \\ &= 100 + (\cdot 054975 \times 100) \\ &= 100 + 5\cdot 4975 \end{aligned}$$

$$\text{Therefore } V_{15} = 105\cdot 4975.$$

The latter process of calculation being the converse of the former, the formula suited to calculations similar to that given in the second example will be

$$V_0 = \frac{V_t}{1 + \cdot 003665 \times t} \dots \dots \dots [2]$$

This formula may evidently be deduced from the last by solving for  $V_0$ , the volume at  $0^\circ$  C.

If now we had 100 liters of gas at  $15^\circ$  C., and it be required to find  $x$ , the volume it would occupy at a higher temperature, say  $25^\circ$  C., we use the following proportion.

$(273 + 15) : (273 + 25) :: 100 : x$  (the vol. at  $25^\circ$ );  
or the calculation may be made by the following approximate formula—

$$V_t' = V_t \left\{ 1 + \cdot 003665 (t' - t) \right\} \dots \dots \dots [3]$$



in which  $V_t'$  represents the volume corresponding to the higher temperature  $t'$ , and  $V_t$  the volume corresponding to the original (lower) temperature  $t$ .

This is the *general formula*—of which [1] is only a special case—for calculating the volume of a gas when *raised* from a lower to a higher temperature. Its converse,

$$V_t = \frac{V_t'}{1 + .003665 (t' - t)} \dots \dots \dots [4]$$

is the *general formula*—of which [2] is only a special case—for calculating the volume of a gas when *reduced* from a higher to a lower temperature.

In this discussion I have made no allusion to pressure, which has an important effect on the volume of a gas, because in these laws and in the formulæ derived from them the pressure is supposed to be *constant*, that is, not to vary.

These laws and formulæ are, therefore, applicable to the expansions and contractions of gaseous volumes *only* when they expand and contract under a constant, or unvarying, pressure, which would always be the case if the expansions and contractions of gases took place only when the mercury in the barometer tube stood at the standard height, 760 m.m. But these expansions and contractions take place at every variation of temperature, whether the barometer reads 760 m.m. or not; moreover, the height of the mercury in the barometer tube, we know from experience, varies considerably at different times in the same day, or even in the same hour, these variations depending on the pressure of the atmosphere—of which the barometer is a measurer; again, the pressure of the atmosphere is found to vary with the height above the *sea level*, at which level the average pressure of a column of it is the same as the weight of a *similar column* of mercury 760 m.m. high; hence it is manifest that if we wish to compare the volumes of gases we must either do

so when measured at the same temperature and pressure ; or, when measured at different temperatures and pressures, calculate the volumes they would occupy, if they had actually been measured off at the same temperature and pressure. The latter course being the most practicable—it being very often inconvenient to wait for the barometer to rise or fall to 760 m.m.—is the one generally adopted ; and the common temperature and pressure, at which all gaseous volumes are compared are, as already stated,  $0^{\circ}$  C. and 760 m.m., of mercury.

Now, there is a very important law derived from experiment, which enables us to connect by means of a formula the volume of a gas with the pressure it supports. I shall call it the third experiment law. It relates to the expansion and contraction of gases under variations of pressure only, and it therefore supposes the temperature to remain constant. It was independently discovered by both Boyle and Marriotte.

*III.—The volume of a gas is inversely proportioned to the pressure it supports ; that is, if the pressure on a gas be doubled, its volume will be reduced to one-half ; if the pressure be halved, its volume will be doubled ; if the pressure be trebled, its volume will be reduced to one-third ; if the pressure be reduced to one-third, its volume will be trebled ; and so on, the volume being always reduced or increased in exactly the same ratio as the pressure is increased or reduced.*

By the aid of this law we can calculate the volume that will be occupied by a gas under any other pressure if we know the volume it occupies under a certain stated pressure. For example—If it be required to know what volume will be occupied by a gas under 760 m.m. barometric pressure, if its volume measured off under a pressure 720 m.m. of mercury were 100 liters :—

The calculation may be made according to the ordinary rule of *inverse proportion*. Since (according to *Law III.*) *the volumes are inversely proportional to the pressures*, the volume at 720 m.m. will be to the volume at 760 m.m. in the *inverse ratio* of these numbers, that is as 760 : 720.

Hence the required volume  $x$  is determined by the following proportion:—

$$760 : 720 :: 100 : x$$

$$\therefore x = \frac{720 \times 100}{760} = 94.74 \text{ liters.}$$

This law may be expressed by a general formula as follows:—If  $V$  denote the volume occupied by a gas under a pressure  $p$ , and  $V'$  its volume under a pressure  $p'$ , then by *Law III.*,

$$V : V' :: p' : p.$$

$$\text{Therefore } V = \frac{V' p'}{p} \dots\dots\dots [5]$$

$$\text{Or, } Vp = V' p' \dots\dots\dots [6]$$

This latter is, I think, the form in which *Law III.* may be most easily retained in the memory. I must therefore ask you not to forget that  $Vp = V' p' = V'' p''$ , &c.

In illustration of this useful formula, I shall work the last example over again; for this purpose let  $V$  represent the volume at 760 m.m.; that is, the volume we require to calculate:  $p$  then will represent 760 m.m.; and  $V'$  will be the known volume (100 liters) at the given pressure 720 m.m. ( $=p'$ ).

Now by formula (6)  $Vp = V' p'$ .

Therefore by substitution  $V \times 760 = 100 \times 720$ .

Hence, as before,  $V = \frac{100 \times 720}{760} = 94.74$ .

The following two laws are also proveable by experiment: they may, however, be deduced as consequences of *Law III*. I shall call them the fourth and fifth experimental laws.

*IV.—The elastic force; or tension, of a gas is directly as the pressure it supports, and inversely as the column it occupies.*

*V.—The density of a gas is directly as the pressure it supports, and inversely as the volume it occupies.*

Since the *elastic force, or tension, of a gas* is measured by the pressure it supports, it is evident that the fourth law is a consequence of the third.

In a similar manner the fifth law may be easily shown to follow from the third.

If now  $V_0$  denote the volume of a *certain quantity* of gas at the temperature  $0^\circ \text{C}$ . (pressure supposed constant), it follows from *Law II.*, commonly known as Gay-Lussac's law, that if  $V_t$  be its volume at the temperature  $t^\circ \text{C}$ .,

$$V_t = V_0 (1 + kt) \dots \dots \dots [7]$$

$$\text{where } k = \frac{1}{273}, \text{ or, } \cdot 003665.$$

$$\text{Hence } V_0 = \frac{V_t}{1 + kt}$$

From Gay-Lussac's law it also follows that if  $V_t'$  be the volume occupied by the *same quantity* of gas, at any other temperature  $t'$

$$V_t' = V_0 (1 + kt').$$

Substituting for  $V_0$  its value from last equation, we have

$$V_t' = V_t \frac{1 + kt'}{1 + kt} \dots \dots \dots [8]$$

Combining this with equation [6] which represents *Law III.*, or that known as Boyle's (or Marriotte's) law, which

states that  $Vp = V'p'$ , it follows that

$$V_t' \times p' = V_t \frac{1 + kt'}{1 + kt} \times p.*$$

That is—

$$V_{p't'} = V_{pt} \frac{1 + kt'}{1 + kt} \cdot \frac{p}{p'} \dots\dots\dots [9]$$

This, which is a combination of Gay-Lussac's and Boyle's laws, is a very useful and important formula: it is applied to calculate the *altered volume* when a gas undergoes a change both of temperature and pressure:  $V_{p't'}$  and  $V_{pt}$  represent the volumes occupied at the pressures and temperatures  $p'$ ,  $t'$  and  $p$ ,  $t$  respectively.

If we replace  $k$  by its equivalent  $\cdot 003665$ , the last formula may be written thus:—

$$V_{p't'} = V_{pt} \frac{1 + \cdot 003665 t'}{1 + \cdot 003665 t} \cdot \frac{p}{p'} \dots\dots\dots [10]$$

Or, substituting the fraction  $\frac{1}{273}$  for  $k$ , and reducing, we may write it as follows:—

$$V_{p't'} = V_{pt} \frac{273 + t'}{273 + t} \cdot \frac{p}{p'} \dots\dots\dots [11]$$

I shall now work out the following problem in illustration of the practical use of such formulæ.

*Problem.*—If the volume of a given quantity of gas be 230 liters when measured at  $14^\circ$  C. and 740 m.m. pressure, what volume will it occupy when measured at the usual standards ( $0^\circ$  C. and 760 m.m.)? To solve this problem we may employ either of the two formulæ just given.

\* For Proof see Addenda.

Employing the latter, we have—

$$\begin{aligned} V_{p't'} &= V_{760,0^\circ} = \text{required Vol.} \\ V_{pt} &= 230 \text{ liters} = \text{given ,,} \\ p' &= 760 \text{ m.m.,} \\ t' &= 0^\circ; \\ p &= 740 \text{ m.m.,} \\ t &= 14^\circ \end{aligned}$$

Therefore we may write our formula thus:—

$$\begin{aligned} V_{760,0^\circ} &= 230 \times \frac{273 + 0}{273 + 14} \times \frac{740}{760} \\ &= \frac{230 \times 273 \times 740}{287 \times 760} \\ &= 213.023 \end{aligned}$$

∴ Required volume = 213.023 liters.

Regnault has found that a *liter of dry air* (at  $0^\circ$  C. and 760 m.m.) weighs 1.293187 gram.

Hence from the general equation

$$V_{p't'} = V_{pt} \cdot \frac{273 + t'}{273 + t} \cdot \frac{p}{p'}$$

we can deduce expressions for the weight of any volume of air—or other gas, whose density with reference to air is known—at any variation both of temperature and pressure.

If  $W$  = the weight in grams of (any volume)  $V$  liters of air at the normal temperature and pressure, then

liter	liters	Wt. in grams of 1 liter	Wt. in grams of $V$ liters
1	: $V$	: : 1.293187	: : $W$
$\therefore V = \frac{W}{1.293187}$			

Substituting this value of  $V$  in the general equation, and writing  $V'$  for  $V_{p't'}$ , we have

$$V' = \frac{W}{1.293187} \cdot \frac{273 + t'}{273 + t} \cdot \frac{p}{p'}$$

Now  $t$  and  $p$  are respectively the temperature and pressure corresponding to the volume  $V$  which was taken at standards : therefore  $t = 0^\circ \text{C.}$ , and  $p = 760 \text{ m.m.}$

Consequently, by making these substitutions, our equation becomes

$$V' = -\frac{W}{1.293187} \cdot \frac{273 + t'}{273 + 0} \cdot \frac{760}{p'}$$

Reducing this expression we obtain

$$V' = 2.1527 W \cdot \frac{273 + t'}{p'} \dots\dots\dots [12]$$

$$\therefore W = \frac{1}{2.1527} \cdot \frac{V' p'}{273 + t'}$$

$$\text{But } \frac{1}{2.1527} = .4645$$

$$\therefore W = .4645 \frac{V' p'}{273 + t'} \dots\dots\dots [13]$$

Since this formula is also true for *any altered volume*  $V''$  when the corresponding temperature and pressure  $t''$  and  $p''$  are substituted for  $t'$  and  $p'$ , it is, therefore, *general* : we may, consequently, remove the accents and write the expression, thus—

$$W = .4645 \frac{Vp}{273 + t} * \dots\dots\dots [14]$$

This important equation enables us to calculate ( $W$ ) the weight in grams of *any volume* ( $V$  in liters) of dry air at any temperature  $t^\circ$  and pressure  $p$  millimeters.

The weight (in grams) of any volume (in liters) of *any other gas* than air is obtained by merely multiplying the

\* From this equation it follows that, for a given mass of gas  $\frac{Vp}{T} =$  a constant, where  $T =$  the absolute temperature, i.e., that measured from  $273^\circ$  below zero (see Addenda). It also follows that, if the weight of the air contained in an *air-thermometer* be .4645 of a gram,  $Vp =$  absolute temperature.

above expression by the specific gravity (with respect to air as unity) of the particular gas whose weight is required.

Hence for *any gas*, if  $s$  = its specific gravity with reference to air as unity—

$$W = .4645 \frac{Vps}{273 + t} \dots\dots\dots [15]$$

The specific gravities of chemical substances, however, are generally stated with reference to hydrogen as unity; we have, therefore, to obtain a formula for the weight of any volume of hydrogen gas, at any temperature and pressure. This can easily be done by substituting for  $s$ , in the last formula, the specific gravity of hydrogen with reference to air as unity, which is 0.0691.

Making this substitution we have

$$W = .4645 \frac{Vp \times .0691}{273 + t}$$

Therefore for *Hydrogen*

$$W = .0321 \frac{Vp}{273 + t} \dots\dots\dots [16]$$

Since the specific gravity, or density, of *any other gas* (with reference to hydrogen) is equal to the atomic, or combining, weight, in the case of an elementary gas, and to half the molecular, or combining, weight in the case of a compound gas, it follows that for any gas

$$W = .0321 \frac{Vp}{273 + t} \left( \frac{\text{combining weight}}{n} \right) \dots [17]$$

where  $n = 1$  for an elementary gas,  
and  $n = 2$  for a compound gas.

By the aid of this all-important formula we calculate the weight corresponding to a given volume of any gas, simple or compound, which obeys the law of (atomic or molecular) volumes, as explained in the preceding lecture—or, conversely, the volume corresponding to any given weight, when its combining weight, temperature, and pressure are known.



I have now directed your attention to those physical laws—derived from experiment—which govern that molecular condition of matter known as the gaseous state. In connection with this subject there remains to be noticed an important physical property of gases, resulting, most probably, from the repulsive molecular movement so characteristic of the gaseous condition. This property is usually called the *diffusion of gases*,—or the process of intermixture of aëriiform substances one with another.

Notwithstanding the great differences in density which exist among gaseous bodies, they are found to intermingle with each other in all proportions, and as freely as if each were a vacuum to the others. Thus, for example, chlorine, which is  $35\frac{1}{2}$  times as heavy as hydrogen, diffuses itself uniformly through the latter gas, even though the hydrogen and chlorine be contained in separate bottles connected together by a long narrow tube—the lighter gas, hydrogen, being uppermost. It is not only that the heavier gas (apparently contrary to the laws of Hydrostatics) ascends through and mingles with the lighter, but likewise the lighter gas descends through and mixes with the heavier one. The mixture thus obtained is mechanical,\* but, unlike the mechanical mixture of two liquids of different densities, such as water and mercury, the mixed gases never again separate into layers differing in density, however long they may be left in a state of rest.

This process of diffusion goes on between gases when separated by porous partitions—such as thin plates of plaster of Paris, animal membranes, &c.—as well as when in immediate contact. It is found by experiment that

\*Provided that the gases be such as do not act chemically on each other when brought together.

the lighter the gas the more rapidly it escapes through porous septa. Thus hydrogen, the lightest of gases, possesses the highest *diffusive power*. The difference between the interdiffusive powers of air and hydrogen may be exhibited by plugging one end of a long glass tube with a thin lamina of plaster of Paris, and, when dry, filling the tube with hydrogen gas. On immersing the open end of this tube—called a diffusion-tube, or diffusiometer—in a vessel containing water (Fig. 6), the water is seen to rise steadily in the tube, in consequence of the hydrogen escaping more rapidly through the porous partition than the air enters to replace it.

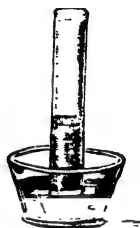


Fig. 6.

It was in this manner that Professor Graham (late Master of the British Mint) discovered that the rate of gaseous diffusion is regulated by a remarkable law, which may be thus stated:—*The relative diffusibility (or velocity of diffusion) of different gases is inversely proportional to the square root of their specific gravities\**; thus it is found that 4 volumes of hydrogen will escape from the diffusion jar in the same time that 1 volume of oxygen is capable of doing so.

Professor Graham has also introduced the term *dialysis*, by which is meant the separation of certain *colloid*† substances (such as hydrated silica, &c.) from more easily diffusible bodies (*crystalloids*) by means of liquid diffusion. Dialysed iron is prepared by this process from moist ferric oxide.

\*The same law regulates the *rate of influx* (into a vacuum) of gases through an orifice in a thin plate. If  $V$  and  $V'$  be the volumes of two gases which pass through a partition in the same time, then

$\frac{V}{V'} = \sqrt{\frac{d'}{d}}$  is the algebraical expression of this law.

† From *Kolle*, glue.

A curious theoretical conclusion may be deduced from the expression  $Vt' = Vt \frac{1 + kt'}{1 + kt}$  (Formula [8], Chapter VIII.) if we suppose the law of diminution of volume (see Experimental Laws I. and II., Chapter VIII.) to hold good while a gas is being cooled down indefinitely : for when  $t'$  equals  $-273^\circ \text{C.}$  this formula becomes (writing  $\frac{1}{273}$  for  $k$ )  $V(-273^\circ) = Vt \frac{273 - 273}{273 + t} = 0.$

Hence the volume of a gas (*supposed incondensable*) becomes zero at the temperature  $-273^\circ \text{C.}$ , i.e. its molecules would then be in actual contact and reduced to a mathematical point :  $-273^\circ \text{C.}$  is therefore the temperature at which no space exists between the molecules of a gas ; and since there is no space for motion to take place, it is probable that there would therefore be no heat in a gas at that temperature, which, for this reason, is called the *absolute zero of temperature*, and may be regarded as the point at which *absolute cold* begins.

Formulae [9], [10] and [11], page 77, may be proved as follows :—

Let  $\phi$  represent the volume assumed at  $t'$  when the volume  $V$  is heated from  $t$  to  $t'$ , then  $\phi = V \frac{273 + t'}{273 + t}$  by Gay-Lussac's law.

If now  $\phi$  be changed to  $V'$  by altering the pressure from  $p$  to  $p'$ , then by Boyle's law—

$$V' : \phi :: p : p' \therefore V' = \phi \frac{p}{p'}$$

And therefore substituting the above value for  $\phi$  we get—

$$V' = V \frac{273 + t'}{273 + t} \times \frac{p}{p'}$$

According to Avogadro's law the molecular volumes of all gases at the same temperature and pressure is one and the same, that is  $\frac{m}{d} = a \text{ constant}$  (where  $m$  is the molecular weight and  $d$  the density)

Hence, for Hydrogen standards  $\frac{m}{d} = 2 = \text{Specific Volume.}$

But for densities referred to air as unity  $\frac{m}{d} = 28.9 = \text{Specific volume,}$  air being 14.44 times as dense as hydrogen.

## CHAPTER IX.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

In this chapter I purpose to direct attention to some *technical terms*, at present much employed in chemical literature, and to explain their scientific meaning.

First, then, I shall endeavour to explain what is meant by the *quantivalence*,\* or *atomicity*, of the Elements.

When we introduce a strip of copper into a solution of argentic sulphate (sulphate of silver), we find that metallic silver separates from the solution, while a certain quantity of the copper dissolves instead of it. And when, into the solution of copper (sulphate of copper) thus formed, a piece of zinc is introduced, metallic copper precipitates, and a fixed portion of the zinc dissolves to replace it.

By experiments of this kind it is found that the *relative proportions by weight* of the metals which thus *replace* each other are (under given conditions) fixed and definite. Thus, for example, for every 108 parts of silver so precipitated 31·75 parts of copper are dissolved to *replace* it ; and for every 31·75 parts of copper thus precipitated 32·5 parts of zinc undergo solution. These being the relative proportions of the metals, silver, copper and zinc, which invariably replace each other whenever such *substitutions* take place, they are termed the *chemical equivalents* of each other. On comparing the numbers 108, 31·75 and 32·5 with those representing the atomic weights of silver, copper and zinc (see Table D, p. 44), we find that the atomic weight and chemical equivalent of silver are the same, whereas the atomic weights of copper and zinc are double their respective equivalents

\* From *quanti* how much, and *valeo* I am worth.

Hence it follows that 1 atom of copper or 1 atom of zinc is equivalent in *replacing power* to 2 atoms of silver; and consequently the action of metallic copper on a solution of silver sulphate ( $\text{Ag}_2 \text{SO}_4$ ) may be expressed by the *chemical equation*—



which shows, at a glance, the fact that 1 atom of copper (Cu), replaces 2 atoms of silver ( $\text{Ag}_2$ ).

In the equivalent substitutions of this nature it is found that while in some cases certain elements replace each other, atom for atom, in other instances, two, three, four, or more atoms of one element are replaced by one atom of another. And thus, taking the *atom of hydrogen* as the *unit of quantivalence*, the several elements are technically termed *monovalent*, *divalent*, *trivalent*, *tetravalent*, &c., according as their individual atoms are capable of replacing, one, two, three, or four, &c., atoms of hydrogen. In this sense, we call hydrogen, chlorine, bromine, iodine, potassium, sodium, silver, &c., *monovalent*, or *monatomic*, elements; oxygen, sulphur, selenium, tellurium, calcium, copper, and zinc, *divalent*, or *diatomic*, elements; nitrogen, phosphorus, arsenic, and gold, *trivalent*, or *triatomic*, elements; and carbon, silicon, tin and platinum, *tetravalent*, or *tetratomic*, elements. The members of these several classes are likewise frequently termed *monads*, *dyads*, *triads*, *tetrads*, &c.

This combining or replacing value of the elementary atoms—termed *quantivalence*, *atomicity*, or *atom-fixing power*—is usually denoted by attaching a corresponding number of dashes to their symbols, thus:  $\text{Ag}'$ ,  $\text{Cu}''$ ,  $\text{Au}'''$ ,  $\text{Pt}''''$ , &c., or by means of Roman numerals, thus:  $\text{Cl}^I$ ,  $\text{O}^{II}$ ,  $\text{N}^{III}$ ,  $\text{C}^{IV}$ .

Under particular conditions the atoms of several of the elements appear to undergo a change of combining value. Thus sulphur, though frequently a dyad element, some-

times acts the part of a hexad. Nitrogen, too, though commonly a triad, occasionally becomes a pentad, as in ammonium chloride ( $\text{NH}_4\text{Cl}$ ). It is generally found that, when the quantivalence of an element varies, the variations are regular, being *all even* or *all uneven*. Thus, for example, sulphur, usually a dyad, may play the part of a tetrad or hexad—but not of a monad or triad. And nitrogen, usually a triad, may become a pentad or monad—but not a dyad, tetrad, or hexad. Elements (like sulphur) of *even* equivalency are termed *artiads*, and elements (like nitrogen) of *uneven* equivalency are called *perissads*.

Another system of marking atomicity has recently been introduced into chemical writings. It consists in attaching lines or dashes (to the number equivalent to the atomicity) to the symbolical notation, and such lines are conveniently termed *bonds*, or *links*. Hydrogen, a monad, is indicated thus  $\text{H}-$ , Oxygen, a dyad,  $-\text{O}-$  and Nitrogen, a pentad, thus  $\text{N}-$  with five bonds, while the sulphur atom as a hexad is written  $-\text{S}-$  with six bonds.

By assuming that these bonds can unite in pairs, thus satisfying each other, it is easy to account for the possibility of an element changing its atomicity in certain combinations. Thus, by one pair of bonds uniting together, sulphur, whose maximum atomicity is hexad, may become a tetrad as in  $\text{SO}_2$ ; and by the union of two pairs of bonds sulphur may become dyad, as in  $\text{H}_2\text{S}$ . Similarly with perissad elements, by the union of pairs of bonds, pentad may become triad or monad:—

Pentad.



Triad.



Monad.



In the following table, the 36 most important elements are classified according to their *maximum* atomicities. The names of the non-metallic elements are here printed in *italics*. Elements resembling each other in chemical characters are grouped together in sections,

Monads, or Monovalent Elements.	Dyads or Divalent Elements.	Triads or Trivalent Elements.	Tetrads, or Tetravalent Elements.	Pentads, or Pentavalent Elements.	Hexads, or Hexavalent Elements.
1st Section.	1st Section.	1st Section.	1st Section.	1st Section.	1st Section.
Hydrogen.	<i>Oxygen</i>	<i>Boron</i> .	<i>Carbon</i> .	<i>Nitrogen</i> .	<i>Sulphur</i>
2nd Section.	2nd Section.	2nd Section.	<i>Silicon</i> . <i>Tin</i> .	<i>Phosphorus</i> . <i>Arsenic</i> . <i>Antimony</i> . <i>Bismuth</i> .	2nd Section.
<i>Fluorine</i> . <i>Chlorine</i> . <i>Bromine</i> . <i>Iodine</i> .	<i>Barium</i> . <i>Strontium</i> . <i>Calcium</i> . <i>Magnesium</i> . <i>Zinc</i> .	<i>Gold</i> .	2nd Section.		<i>Chromium</i> . <i>Manganese</i> . <i>Cobalt</i> . <i>Nickel</i> . <i>Iron</i> .
3rd Section.	3rd Section.		3rd Section.		
<i>Potassium</i> . <i>Sodium</i> .	<i>Cadmium</i> . <i>Mercury</i> . <i>Copper</i> .		<i>Platinum</i> .		
4th Section.			4th Section.		
<i>Silver</i> .			<i>Lead</i> .		

The atom of iron in ferric compounds has tetratomicity.

The number of bonds of any atom in apparent play in a chemical compound is termed the *active* atomicity, while the number of bonds which have disappeared by mutual union is known as the *latent* atomicity.

∴ *Absolute* atomicity = *active* + *latent*.

The term *radicle* (from *radix*, a root), is applied to any atom or group of atoms which, for the time being, may be considered as forming the principal atomic component\* of the molecule of any compound body. Accordingly, we have simple and compound radicles. The elementary atoms are *simple radicles*; and those groups of two, or more, simple radicles (or atoms) which, like the elementary atoms, can pass from one substance to

\* Thus *Ag*. would be the principal atomic component of the *silver* compounds.

another *without undergoing decomposition*, are called *compound radicles*. The term *atom* is frequently applied to compound radicles in the same sense as it is to the elements. Thus we speak of  $\text{NH}$ , as an atom of the compound radicle ammonium, and justly so, since it is capable of replacing an atom of potassium or of sodium.

Radicles are divided into two great classes :

*Acid Radicles*.—Those which are electro-negative ; and

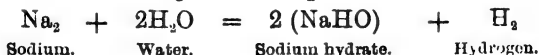
*Basic Radicles*.—Those which are electro-positive.

Among simple radicles the non-metallic atoms constitute the principal acid radicles, while the metallic atoms are generally basic radicles. Hydrogen forms a kind of link between the two groups—its atom being, usually basic when in combination with non-metallic atoms, and acid when combined with metallic atoms.

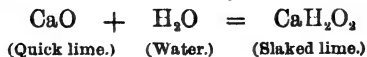
The electro-positive elements, or the metals, and the electro-negative elements, or the non-metals, together with about twenty compound radicles, constitute respectively the *basic* and *acid* radicles with which we shall have to deal (*See Table G, p. 97*).

When the elements of water enter into combination with a metal or its oxide, the resulting compound is called a *hydrate*—thus metallic sodium and water yield sodium hydrate and free hydrogen.

The chemical change is thus represented :—



And calcium oxide and water yield Calcium hydrate



The term *salt*, which in ordinary language is used to denote sodium chloride, or common sea-salt, is applied by all chemists to all those compound bodies which



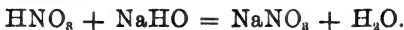
(unlike compound radicles) as a rule *undergo decomposition* previous to entering into further chemical combinations.\*

The term *acid*—originally the generic name for those bodies which (like vinegar and lime-juice) possess a sharp or sour taste—is now employed, in a wider sense, to designate compounds containing one or more atoms of hydrogen *displaceable* by metallic atoms or by basic compound radicles.

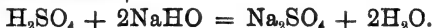
Acids react with many compound bodies in the same way that salts do, viz., by double decomposition, *e.g.* :—  
Potass. hydrate + Hydrochloric acid = Potass. chloride + Water



Again nitric acid and sodic hydrate yield the salt sodic nitrate and water—



And sulphuric acid and sodic hydrate give sodic sulphate and water.†



We may therefore, define an acid, in general terms, as a *salt of hydrogen*. On the other hand, a salt may be regarded as *derived* from an acid, in which one or more atoms of hydrogen have been exchanged for an equivalent number of metallic atoms or compound basic radicles.

The acids are said to be *monobasic*, *dibasic*, *tribasic*, &c., when their representative molecules contain respectively *one*, *two* or *three*, &c., displaceable atoms of hydrogen :—

Nitric acid ( $\text{HNO}_3$ ), Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) are respectively mono-, di- and tri-basic acids.

\* If we try now to state what is the idea which is attached to the word salt, as at present used in chemical science, we find it impossible to do so in very precise terms. Probably we may most correctly define this idea by saying that it implies the capability of readily undergoing *double decomposition*.—*Watts' Dict. Chem.*

† In fact the modern *criterion* of an acid is that when acted upon by a metallic hydrate it should yield a salt with the elimination of water, as in the above examples.

The term *base* is applied to an important class of compound bodies—opposed in chemical properties to the acids—which by uniting with acids form salts.\*

The metallic *oxides* and their *hydrates* form the principal inorganic bases.

The following bodies serve as illustrations:—

*Basic Oxides.*

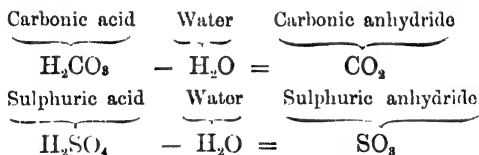
*Hydrates.*

Sodic oxide (soda) $\text{Na}_2\text{O}$ ;	Sodic hydrate (caustic soda) $\text{NaHO}$ .
Potassic oxide (potash) $\text{K}_2\text{O}$ ;	Potassic hydrate (caustic potash) $\text{KHO}$ .
Calcic oxide (quicklime) $\text{CaO}$ ;	Calcic hydrate (slaked lime) $\text{CaO.H}_2\text{O}$ .
Magnesian oxide $\text{MgO}$ ;	Magnesian hydrate $\text{MgH}_2\text{O}_2$ .
Ferric oxide $\text{Fe}_2\text{O}_3$ ;	Ferric hydrate $\text{Fe}_2\text{H}_6\text{O}_6$ .
Aluminic oxide $\text{Al}_2\text{O}_3$ ;	Aluminic hydrate $\text{Al}_2\text{H}_6\text{O}_6$ , &c., &c.

The most prominent character of a base is its *capacity for saturating acids*. In this respect the powers of bases differ considerably.

Certain compounds of nitrogen and hydrogen, hydrogen and phosphorus, &c., as ammonia ( $\text{NH}_3$ ) and phosphuretted hydrogen ( $\text{PH}_3$ ) are sometimes classed among the bases †

The term *anhydride* is employed to designate the compound which remains after all the displaceable hydrogen is removed (in the form of water) from one of the ordinary *oxygen acids*. Thus—



\* According to the *binary theory of salts*, all bodies resulting from the combination (*in pairs*) of acid and basic radicles are classed as salts. Thus an acid is the *electro-negative* constituent of a salt while a base is the *electro-positive* constituent.

† This type of basic bodies belongs principally to *Organic Chemistry*, which, according to Liebig, is 'the chemistry of compound radicles.'

When an acid and a base combine a salt is always produced. If such a salt be the result of the union of an *oxygen-acid* with a base it is termed an *oxysalt*; if the salt contain sulphur instead of oxygen it is known as a *sulpho-salt*; and when free from oxygen and sulphur it is called a *haloid-salt*, is derived from a halogen acid, such as the hydrochloric, hydrobromic, hydriodic or hydrofluoric.

An *anhydro-salt* is formed when the anhydride of the acid of the salt enters into combination with the ordinary salt:—for example,  $K_2CrO_4, CrO_3$  is called anhydrochromate of potassium.

*Oxy-salts* are, according to constitution, divisible into three classes, *normal*, *acid*, and *basic*:—

A *normal salt* is one in which the whole of the displaceable hydrogen of the acid is exchanged for an equivalent amount of metal or of basic compound radicle.

An *acid salt* is one in which only a portion of the displaceable hydrogen is displaced by a metal or by a compound basic radicle,—some of the hydrogen of the acid from which the salt is derived being still present, it is constitutionally looked upon as an acid salt, even though it may have an alkaline reaction; bicarbonate of soda for example  $NaHCO_3$ , now called *acid carbonate*.

A *basic salt* may be regarded as a compound resulting from the combination of a normal salt with an additional quantity of its own or some other basic substance; a salt in which the units of basicity exceed the units of acidity; it is the opposite of an anhydro salt.

All acids (soluble in water) *taste sour* and turn vegetable *blue* colours *red*. The soluble bases possess an *acid* taste and restore the *blue* colour to vegetable blues which have been reddened by an acid. Bases turn *yellow* turmeric *brown*, while acids restore the *yellow* colour to turmeric which has been browned by a base.

The *alkalis*\* are characterized by being more soluble in water than other bases, and by their power of neutralizing† acids; their solutions, like those of other bases, restore the blue colour to reddened litmus, but turn the infusion of purple cabbage *green*.

A salt has an *acid reaction* when it turns litmus solution *red* and a *basic reaction*‡ when it turns reddened litmus *blue*. A *neutral salt* does neither. The reaction of a solution of any salt with litmus is not always in accordance with its constitution; for instance, a normal salt may have an acid or a basic reaction notwithstanding the apparent neutrality of its normal constitution. The reaction of a salt cannot, therefore, be predicted by its molecular constitution, but is determined by experiment.

Here is a list of various kinds of salts, showing their modes of derivation from corresponding acids:—

<i>Acids.</i>	<i>Derived Salts.</i>
<i>Monobasic</i> Hydrochloric, $\text{HCl}$	{ Potassium Chloride, $\text{KCl}$ . Sodium Chloride, $\text{NaCl}$ . Ammonium Chloride, $\text{NH}_4\text{Cl}$ . &c. &c.
<i>Monobasic</i> Nitric Acid, $\text{HNO}_3$	{ Potassium Nitrate, $\text{KNO}_3$ . Silver Nitrate, $\text{AgNO}_3$ . &c. &c.
<i>Di-basic</i> Carbonic Acid, $\text{H}_2\text{CO}_3$ ( <i>Hypothetical</i> )	{ $\text{Na}_2\text{CO}_3$ (Normal) $\text{NaHCO}_3$ (Acid)

\* The term *alkali* is of Arabic origin—*al* signifying *the*, and *kali*, the name of the plant from the ashes of which the vegetable alkali, caustic potash, was obtained. The alkalis proper are *potash* (the vegetable alkali), *soda* (the mineral alkali), and aqueous *ammonia* (the animal alkali).

† A substance is termed *neutral* when it exhibits neither acid nor basic reaction with litmus solution.

‡ Basic reaction is more frequently termed *alkaline reaction*, the alkalis being themselves strongly basic in character.

<i>Acids.</i>	<i>Derived Salts.</i>
<i>Di-basic</i>	
Sulphuric Acid, $\text{H}_2\text{SO}_4$	$\left\{ \begin{array}{l} \text{Na}_2\text{SO}_4 \text{ (Normal)} \\ \text{NaH SO}_4 \text{ (Acid)} \end{array} \right.$
<i>Tri-basic</i>	
Phosphoric Acid, $\text{H}_3\text{PO}_4$	$\left\{ \begin{array}{l} \text{Na}_3\text{PO}_4 \text{ (Normal)} \\ \text{Na}_2\text{HPO}_4 \text{ (Acid)} \\ \text{NaH}_2\text{PO}_4 \text{ (Acid)} \\ \text{Ca}_3(\text{PO}_4)_2 \text{ (Normal)} \\ \text{CaH}_4(\text{PO}_4)_2 \text{ (Acid)} \\ \text{\&c.} \end{array} \right.$
<i>Tetra-basic</i>	
Silicic Acid, $\text{H}_4\text{SiO}_4$	$\left\{ \begin{array}{l} \text{Na}_4\text{SiO}_4 \\ \text{K}_4\text{SiO}_4 \end{array} \right.$

The majority of the natural silicates do not, however, conform to this simple law of derivation from silicic acid.

Gerhardt has instituted a system of classifying chemical compounds according to certain *types*\*—which are molecular models, or patterns, from one or other of which the molecules of every compound may be supposed to be derived by the process of *equivalent substitution*.

The typical bodies are four in number, namely :—

- |                               |   |                              |
|-------------------------------|---|------------------------------|
| (1) Hydrochloric acid type... | $\left. \begin{array}{c} \text{H} \\ \text{Cl} \end{array} \right\}$                        | , or $\text{HCl}$ .          |
| (2) Water type.....           | $\left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\}$                         | O, or $\text{H}_2\text{O}$ . |
| (3) Ammonia type .....        | $\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \end{array} \right\}$             | N, or $\text{H}_3\text{N}$ . |
| (4) Marsh-gas type.....       | $\left. \begin{array}{c} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right\}$ | C, or $\text{H}_4\text{C}$ . |

Compounds, the molecules of which are similarly constituted, and which exhibit similar chemical reactions, are said to belong to the *same type*, and they are supposed to be derived from that type by substitution, and for this reason are not unfrequently called *substitution products*.

\* From *τύπος* (*typos*), a model.

In this sense the chlorides, bromides, iodides, &c., are regarded as belonging to the same type, viz. the

*Hydrochloric acid type*.....H Cl.

Thus, for example, when K is substituted for H in this typical molecule, we get K Cl, a molecule of chloride of potassium. Potassium bromide and iodide (K Br and KI) are similarly derived.

Some compound bodies must be regarded as derived from a *multiple type*. Calcium chloride,  $\text{Ca}''\text{Cl}_2$ , for instance, is built on the

*Double hydrochloric acid type*...  $\left\{ \begin{smallmatrix} \text{H}_2 \\ \text{Cl}_2 \end{smallmatrix} \right.$

two atoms of hydrogen being replaced by the divalent atom  $\text{Ca}''$ .

The oxides, sulphides, oxygen salts, sulpho salts, &c., belong to the *water type*,  $\text{H}_2\text{O}$  and its multiples  $n\text{H}_2\text{O}$ .

Thus a monobasic oxygen acid, as, for example, nitric acid, may be regarded as derived from the water type by the replacement of one of the hydrogen atoms in the water molecule  $\left\{ \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$  by the compound radicle  $\text{NO}_2$ .

*Nitric acid*.....  $\left\{ \begin{smallmatrix} \text{H} \\ \text{NO}_2 \end{smallmatrix} \right\} \text{O}$

and potassium nitrate on this theory would be written thus :  $\left\{ \begin{smallmatrix} \text{K} \\ \text{NO}_2 \end{smallmatrix} \right\} \text{O}$ , where the metal displaces the only atom of hydrogen in the monobasic acid  $\text{HNO}_3$ . Hence monobasic acids can yield but one class of salts, *i.e.* normal salts ; while di-basic acids yield two kinds of salts and tri-basic acids three kinds, as in the case of the phosphates of sodium (p. 92).

Bodies belonging to the remaining two types are mostly represented by organic compounds.

When the formula of a chemical compound indicates, by means of the lowest integer numbers, merely the *relative proportions* in which the several elementary atoms of which it is composed are associated, it is termed an *empirical formula*. If a chemical formula expresses the *absolute number* of the several elementary atoms entering into the composition of a single molecule, it is then called a *rational formula*. Thus the two formulæ of ferric chloride are written :—

Empirical formula..... $\text{Fe Cl}_3$

Rational formula..... $\text{Fe}_2 \text{Cl}_6$

True molecular formulæ\* are necessarily rational formulæ. Empirical formulæ are (or should be) only employed to represent compounds, the true molecular weights of which remain undetermined.

The empirical formula of a compound is easily determined when we know its *percentage composition*. The manner in which this is usually done is to divide the percentage amount (ascertained by analysis) of each constituent by its combining weight, then dividing each of the quotients thus obtained by that which is least, thus finally reducing to their simplest ratios.

For example:—A compound is found on analysis to possess the following percentage composition; we deduce the empirical formula as follows :—

Hydrogen.....17·647

Nitrogen .....82·353

Total=100·000

Proportion of Hydrogen Atoms =  $\frac{17·647}{1} = 17·647$

Proportion of Nitrogen Atoms =  $\frac{82·353}{14} = 5·882$

\* Compare Chapter VII., page 59.

The simplest ratio between 17·647 and 5·882 is 3 : 1—  
for  $17·647 \div 5·882 = 3 \div 1$ .

Therefore the empirical formula is (H=3 atoms, and N=1 atom)  $H_3N$ , that is Ammonia.

As another example of this oft-required process, let it be required to determine the empirical formula of a substance composed of hydrogen, carbon and oxygen, which yields by analysis the following percentage composition, *viz.* :—

Hydrogen.....	2·00
Carbon .....	42·00
Oxygen.....	56 00

Total = 100·00

Now  $\frac{2·00}{1} = 2 = \text{Proportion of Hydrogen atoms ;}$

$\frac{42}{12} = 3·5 = \text{Proportion of Carbon atoms ;}$

and  $\frac{56}{16} = 3·5 = \text{Proportion of Oxygen atoms,}$

The simplest whole numbers in the same ratio are 4, 7 and 7  $\therefore$  the empirical formula is  $H_4C_7O_7$ , that is meconic acid (an acid found in opium).

On the other hand, when the formula of a body is known, we may have to determine its percentage composition. This may be done as follows:—

Suppose we were asked to calculate the percentage composition of the salt whose formula is—

$Na_2HPO_4$  (disodium-hydrogen phosphate)

Then we know that  $\left\{ \begin{array}{l} Na_2 = 46 \\ H = 1 \\ P = 31 \\ O_4 = 64 \end{array} \right.$

Therefore the molecular weight of the salt } = 142



Hence by proportional parts we have—

142 : 100	46 : 32·4 = Sodium	
142 : 100	1 : 0·7 = Hydrogen	
142 : 100	31 : 21·8 = Phosphorus	)
142 : 100	64 : 45·1 = Oxygen	

∴ The salt contains in every 100 parts by weight

Sodium.....	32·4	parts
Hydrogen.....	0·7	„
Phosphorus.....	21·8	„
Oxygen.....	45·1	„
<hr/>		
Total.....	100·0	

Concerning every variety of matter there are *three things* which the Chemist desires to ascertain:—

*First*:—The nature, or *quality*, of its constituents.

*Second*:—The proportion, or *quantity*, of its constituents.

*Third*:—The mode of *arrangement* of its constituents.

Analytical Chemistry deals with the *first* and *second* under the titles of *Qualitative* and *Quantitative* Analysis; while the *third* involves considerations of a purely speculative character—*theory*.

- Table G. (opposite) gives a classification of the principal inorganic salt-forming radicles.

**TABLE G.**  
**CLASSIFICATION OF RADICLES.**

Basic Radicles.			Acid Radicles.		
Names.	Symbols.	Combining Weights.	Names.	Symbols.	Combining Weights.
<i>Simple.</i>			<i>Simple.</i>		
Hydrogen (a) ..	H	1	Chlorine .....	Cl	35.5
Potassium ....	K	39	Bromine .....	Br	80
Sodium .....	Na	23	Iodine .....	I	127
Lithium .....	Li	7	Fluorine .....	F	19
Barium .....	Ba	137	Oxygen .....	O	16
Strontium ....	Sr	87.5	Sulphur.....	S	32
Calcium .....	Ca	40	Nitrogen .....	N	14
Magnesium ....	Mg	24	Boron .....	B	11
Aluminium ....	Al	27	Phosphorus ....	P	31
Chromium ....	Cr	52.5	Carbon .....	C	12
Iron .....	Fe	56	Silicon .....	Si	28
Manganeseum ..	Mn	55	<i>Compound (b)</i>		
Zinc .....	Zn	65	Cyanogen .....	(CN)=Cy	26
Cobalt .....	Co	59	Ferrocyanogen..	(FeCy <sub>5</sub> )	134
Nickel .....	Ni	59	Ferricyanogen ..	(Fe <sub>3</sub> Cy <sub>6</sub> )	268
Cadmium .....	Cd	112	Sulphocyanogen	(CNS)	58
Copper .....	Cu	63.5	Nitric radicle.	(NO <sub>3</sub> )	62
Silver.....	Ag	108	Chloric ..	(ClO <sub>3</sub> )	83.5
Mercury .....	Hg	200	Iodic ..	(IO <sub>3</sub> )	175
Lead .....	Pb	207	Sulphurous ..	(SO <sub>3</sub> )	80
Bismuth .....	Bi	210	Hyposulphurous	(S <sub>2</sub> O <sub>3</sub> )	112
Tin.....	Sn	118	Sulphuric ..	(SO <sub>4</sub> )	96
Antimony.....	Sb	122	Silicic ..	(SiO <sub>4</sub> )	92
Arsenicum ....	As	75	Fluosilicic ..	(SiF <sub>6</sub> )	142
Gold .....	Au	196.5	Carbonic ..	(CO <sub>3</sub> )	60
Platinum .....	Pt	197	Oxalic ..	(C <sub>2</sub> O <sub>4</sub> )	88
<i>Compound (b)</i>			Boracic ..	(BO <sub>3</sub> )	59
Ammonium ....	1(NH <sub>4</sub> )	18	Phosphoric ..	(PO <sub>4</sub> )	95
	=Am		Chromic ..	(CrO <sub>4</sub> )	116.5
			Arsenious ..	(AsO <sub>3</sub> )	123
			Arsenic ..	(AsO <sub>4</sub> )	139

(a) The difference between *Basic* and *Acid* Radicles is rather one of degree than of kind.  
 (b) The idea of compound radicles, as it is now entertained, is quite independent of the question whether they can be actually prepared in the separate state or not. A radicle, in modern chemical language, is simply a group of elements, which is common to a more or less numerous series of allied compounds, and remains unaffected by the processes whereby these compounds are transformed one into another.—*Watt's Chem. Dict.*

## CHAPTER X.

### CHEMICAL PHILOSOPHY—GENERAL PRINCIPLES.

The crust of our Earth is composed of rocks and minerals, which by natural decay produce the soils, on which grow the plants that provide sustenance for animal life.

A *mineral* is best defined as an inorganic substance having a definite chemical composition and a distinct geometric form.\* Rocks and stones are composed of aggregates of minerals. Minerals are definite chemical compounds ; while rocks are usually mechanical mixtures of mineral substances, though in a few instances a single mineral substance forms the sole component of some kinds of rock, such as pure limestone, quartz rock, &c.

As an example of a mineral, I may mention *Calcite*, which is found crystallized in certain distinct geometric shapes, and it also possesses the following definite percentage composition :—

Calcium oxide 56 parts by weight.

Carbon di-oxide 44        "        "

---

100

On the other hand, a specimen of rock will not possess a particular geometric form, and its composition will be represented by a variety of bodies, each of which is in itself a separate mineral substance. Thus granite rock contains the minerals quartz, felspar and mica, in varying

\* When occurring in the free and unmixed condition.

proportions—the mica may even be absent or replaced by another mineral without destroying the granitoid nature of the rock.

Hence we see that Mineralogy—the science of Minerals—may be regarded from the twofold aspect of (a) chemical composition and (b) geometric form.

The former is entirely under the domain of Chemistry, but the latter belongs to the kindred branch of Science known as Crystallography.

All solid substances are either *crystalline* or *amorphous*—crystalline when occurring in regular geometric forms (termed crystals), *e.g.* crystallized quartz (rock crystal), salt, calc-spar, &c.; *amorphous*\* when occurring without regular, geometric form, *e.g.* massive quartz (quartz rock), chalk, slate, &c.

Crystals are geometric solids bounded by plane surfaces having definite geometric relations to each other, for the complete study of which I must, at present, refer you to some of the standard works on Crystallography.†

Though the number and variety of crystalline forms are very considerable, yet by careful study of their characteristic properties, all the known natural or artificial substances can be grouped under a comparatively small number of classes, or systems.

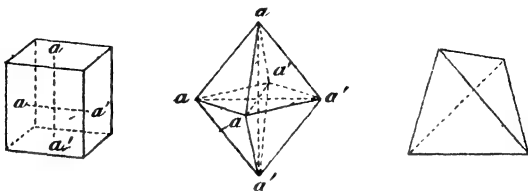
The following simple figures represent *open* and *closed* forms in each of the systems—*prisms* and *pyramids*—symmetrically arranged around axes. The tetrahedron and rhombohedron are *hemiheral* forms—*aa'*, *bb'*, *cc'*, &c., represent the axes.

\* From a not,  $\mu\omicron\rho\phi\eta$  form.

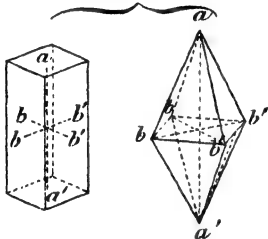
† With the assistance of the *models of crystalline forms* which you see before you on the Lecture Table, we shall study briefly the principal crystallographic laws.

# CRYSTALLINE SYSTEMS.

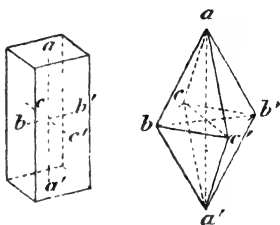
## *Monometric*



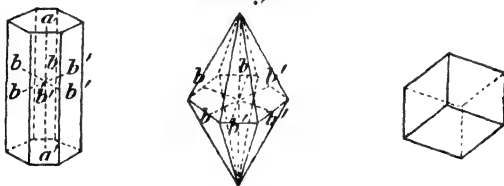
## *Dimetric*



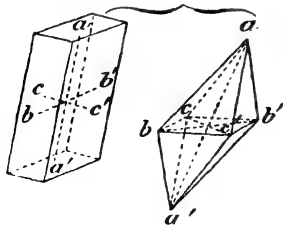
## *Trimetric*



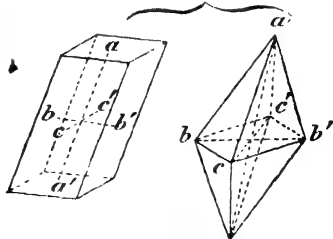
## *Hexagonal*



## *Monoclinic*



## *Triclinic*



The following seven groups of classes represent all the possible crystalline systems in which organic or inorganic crystalline substances can possibly occur :—

*Crystalline Systems.*

1. The Monometric (regular, or cubic) System.
2. The Dimetric (square, prismatic, or pyramidal) System.
3. The Trimetric (right prismatic, or rhombic) System.
4. The Monoclinic (or oblique prismatic) System.
5. The Diclinic System (*not known in nature*).
6. The Triclinic (or doubly oblique) System.
7. The Hexagonal (or rhombohedral) System.

These several systems may be classified under three distinct groups, as under :—

A. The Metric Group (having 3 axes all at right angles. {

1. Monometric—axes of *one* length.
2. Dimetric—axes of *two* lengths.
3. Trimetric—axes of *three* lengths.

B. The Clinic Group (having 3 axes making one or more *acute* angles).

4. Monoclinic—one acute angle between axes.
5. Diclinic—*two* acute angles between axes.
6. Triclinic—*three* acute angles between axes.

C. The Hexagonal (having 4 axes).

7. Hexagonal—three axes equal and in same plane and one perpendicular to plane of those three.

When the same substance forms crystals of two different Systems, it is said to be *dimorphous*,\* *e.g.* carbon, sulphur, calcium carbonate, &c. When two different substances form crystals of the same kind, they are said to be *isomorphous* (*ἴσος*, *isos*, equal, and *μορφή*, *morphé*, shape, or form), *e.g.* Iceland spar and Pearl spar, &c. Isomorphous substances can usually replace each other in compounds without destroying the identity

\* A substance occurring in three systems is *trimorphous*.

of the particular species—thus *iron*, *chromium* and *aluminum* replace each other in the *alums*, which are usually double sulphates of an alkali metal and one or other of these three metals.\* Isomorphous substances have approximately the same specific volume.

Bodies which consist of the same ingredients, associated in the same relative proportions—i.e. have the same percentage composition—and which are yet regarded as distinct from each other, in consequence of differing essentially in properties, are termed *isomeric*† bodies. *Acetylene*,  $C_2H_2$ , and *Benzene*,  $C_6H_6$ , are examples of isomerides. Such bodies are divisible into *polymeric* and *metameric* isomerides. Benzene is evidently a polymer of acetylene, its formula being a multiple of that of acetylene, for  $C_6H_6 = 3(C_2H_2)$ . Isomerides having the same molecular weight, but whose component atoms are differently arranged, are termed *Metamerides*, as for example *Urea*,  $CH_4N_2O$  and *Ammonium cyanate*,  $NH_4CNO$ .

When an elementary body occurs in two or more distinct forms possessing different properties, it is said to be *allotropic*. Allotropy is unexplainable except on the assumption that atoms of the same element are capable of combination among themselves so as to form different groups of atoms of the same element (as for example Oxygen  $O_2$  and Ozone  $O_3$ ) with different properties.

The affinities of elementary substances are noted to be greater at the moment of being set free from combination‡ than afterwards. This is probably due to the recombination of individual atoms (afterwards) to form molecules

\*The relative weights of the replaced and replacing substances are always in the ratio of their chemical equivalents. This holds good for all kinds of replacements of isomorphous bodies.

†From *ἴσος* equal, and *μέρος* a part.

‡At this particular moment an element is said to be in the *nascent* state (*nascens*, being born).

## Names of Familiar Minerals occurring in different Crystalline Systems.

Monometric.	Dimetric.	Trimetric.	Monoclinic.	Triclinic.	Hexagonal.
Iron Pyrites. Fluor Spar. Rock Salt. Galena. Alum. Diamond. Garnet. Native Gold. Native Copper. Magnetic Oxide. Spinel Ruby. Grey Copper (ore). Leucite.	Copper Pyrites. Tin Stone. Apophyllite. Zircon. Rutile. Idocrase.	Aragonite. Topaz. Stilbite. Sulphur. Heavy Spar. Orpiment. Andalusite.	Orthoclase Felspar Sanidine. Gypsum. Sulphate of Iron. Augite. Hornblende. Wolfram. Sodium Carbonate. Realgar.	Albite. Labradorite. Anorthite. Copper Sulphate. Axinite. Oligoclase Felspar.	Calc Spar. Apatite. Quartz. Corundum. Beryl. Tourmaline. Mimetite.



To assist in the identification of Minerals, mineralogists employ the following "Scale of Hardness":—

Degree of Hardness.	Represented by
1	Talc.
2	Selenite (crystallised Gypsum).
3	Calc spar.
4	Fluor spar.
5	Apatite.
6	Orthoclase (Felspars).
7	Quartz (Rock Crystal).
8	Topaz.
9	Sapphire (Corundum).
10	Diamond.

The French employ a similar scale with the numbers in the inverse order.

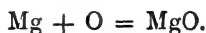
In addition to crystalline form and hardness, the accurate determination of the *relative density* (or physical specific gravity) of a mineral provides another useful test for its recognition. The following formula serves the purpose of calculation :—

$$\text{Relative Density} = \frac{\text{Weight of Substance}}{\text{Weight of equal Volume of Water}}$$

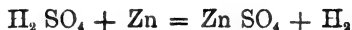
By general agreement the *specific gravities* of solids and liquids are referred to water (taken as unity) as their standard. *Hydrometers* are used for ascertaining the specific gravities of liquids.

The *modes* of chemical change, though apparently of great variety and complexity, may yet be reduced to six distinct groups of cases, thus :—

CASE I.—*Changes by direct union, or simple combination: as, for example, when powdered antimony combines with chlorine; or when magnesium ribbon burns in oxygen.*

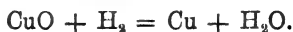


CASE II.—*Changes by displacement, or substitution: illustrated by the displacement of hydrogen, from sulphuric acid, by zinc.*

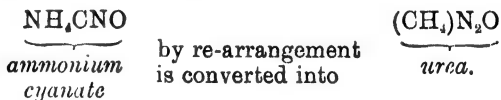


This change is utilized in the preparation of Hydrogen.

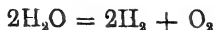
CASE III.—*Changes by reduction: as when an oxide is reduced by hydrogen.*



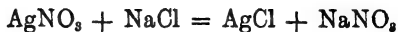
CASE IV.—*Changes by re-arrangement (isomeric changes). Such changes may be illustrated by the coagulation of the white of an egg on boiling; or perhaps better still by the change which ammonium cyanate undergoes in becoming converted into urea.*



CASE V.—*Changes by simple decomposition, or resolution: illustrated by the decomposition of water by dissociation or by means of an electric current.*



CASE VI.—*Changes by double decomposition: illustrated by the exchange of radicles of two salts in solution: as, for example, silver nitrate and sodium chloride.*



Berthollet has given us two very convenient *Rules* for predicting the double decomposition of salts, *viz.*:—

*Rule 1.*—If the acid radicle of the one salt with the basic radicle of the other would form a more *insoluble* compound than either of the given ones, then double decomposition will ensue on mixing their solutions:—



Table H now may be consulted with advantage to ascertain the solubility or *insolubility* of salts in water, which knowledge enables the chemist to predict cases of double decomposition. The insolubility of barium sulphate accounts for the above reaction.

*Rule 2.*—Two bodies mixed (or heated) together will decompose each other if it be possible by double decomposition to produce a more *volatile* body than either of the original bodies.

When ammonium sulphate and barium chloride are *heated* together double decomposition ensues owing to the *volatility* of the ammonium chloride.



Similarly, when hydrochloric acid is poured over chalk immersed in water, we have a case of *volatility* in the escape of carbonic acid gas.



**TABLE II.**  
**SOLUBILITY OR INSOLUBILITY (IN WATER) OF SALTS OF THE PRINCIPAL METALS.\***

	<i>Hydrate.</i>	Arsenate.	Arsenite.	Carbonate.	Chloride.	Chromate.	Cyanide.	Iodide.	Nitrate.	Oxalate.	Phosphate.	Sulphate.	Sulphide.	Sulphite.	REMARKS.
<i>Ammonium</i> .....	S	S	S	S	S	S	S	S	S	S	S	S	S	S	<p>In this Table S stands for <i>Soluble</i>, I " " <i>Insoluble</i>. s.S " <i>sparingly Soluble</i>. I.S is used where the <i>proto</i> salt is <i>insoluble</i> while the <i>per</i> salt is <i>soluble</i>. The dash(—) is used in untried cases, or where such salts are unknown. The relative solubility will be found at the intersection of the horizontal and vertical columns.</p>
Aluminum .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Antimony .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Barium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Bismuth .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Cadmium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Calcium .....	S	I	I	I	S	I	I	I	S	S	I	I	I	I	
Chromium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Cobalt .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Copper .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Iron .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Gold .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Lead .....	S	I	I	I	S	I	I	I	S	S	I	I	I	I	
Magnesium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Manganese .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Mercury .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Nickel .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Platinum .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Potassium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Silver .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Sodium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Strontium .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Tin .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	
Zinc .....	I	I	I	I	S	I	I	I	S	S	I	I	I	I	

\* Consult the Author's Test Tables for Qualitative Analysis.

## CHAPTER XI.

### HYDROGEN.

**H = 1 ; Density = 1 ; Atomicity = 1.**

*Sp. gr. (air = 1) = 0.0691.*

**History.**—In the sixteenth century Paracelsus observed that a gas, which he took to be air, was evolved when iron is dissolved in sulphuric acid. Hydrogen was first recognized as an independent body in the year 1766. The credit of its discovery is given to Cavendish by some, and to Watt by others. Cavendish called it *inflammable air*.

**Occurrence.**—This element acquires its name from its occurring as one of the components of water (ὕδωρ, water, and γεννάω, I produce). Though seldom found free, or uncombined, in nature, it occurs in the free state amongst volcanic gases. It constitutes *one-ninth* part by weight of all the water on the globe ; it exists in all vegetable and animal substances ; it is also a constituent of nearly all combustible materials, as coal, candles, oils, gas, &c., and of all acids whatsoever.

**Properties.**—We shall now consider the chief characteristic properties of hydrogen gas ; they are—

1st. Its combustibility, or inflammability in air.

2ndly. Its levity, or lightness.

These properties may be demonstrated by the following experiments:—I have here, standing on the shelf of the pneumatic trough, some jars of hydrogen gas ; and, in order to exhibit its combustibility in air, I shall take one of these

in my left hand, holding it still with its mouth downwards, and with the other hand pass an ignited taper up into the jar; when this is done you will observe that the *gas burns* (with a very pale and scarcely visible flame) *only at the surface, or where it is in contact with the air, and that the taper becomes extinguished*, but on withdrawing it from the jar it is *rekindled at the surface of contact of the hydrogen and air*. Now I shall perform a similar experiment, using another jar with its mouth held upwards; in this case you notice that the gas burns with a slight explosion and with an ascending flame.

As illustrations of the extreme levity of hydrogen the following experiments will suffice:—

I have here an air-tight bag to which is fitted a brass pipe, similar to a tobacco pipe, which is furnished with a stop-cock (Fig. 7). This bag has been filled with hydrogen gas which was prepared previous to



Fig. 7.

lecture—it was liberated from hydrogen sulphate by the action of zinc in the mode to be described. I immerse the brass pipe in this solution of soap (prepared by rubbing a piece of soap in a small quantity of distilled water till the mixture gets very frothy). I now open the stop-cock, and by pressing the bag gently, blow soap-bubbles with the hydrogen gas. These miniature balloons ascend to the ceiling of the room after they are detached from the pipe, thereby proving that they are lighter than the air in which they float.

The second property may be illustrated in a more striking manner by filling a small balloon of collodion or of gold-beaters' skin with hydrogen; for this purpose the hydrogen should be dried by passing it through a tube packed with fragments of quicklime or hydrate of

potassium, by either of which it is deprived of its moisture, and is thus rendered specifically lighter. The balloon may be filled either from a large transferring jar, full of hydrogen, by pressing the jar down into the water of the pneumatic trough, and thus forcing the gas through the drying tube and into the balloon; or by attaching it—interposing a drying tube—to the bottle for generating hydrogen. When properly filled, the balloon must be fastened round the neck with a fine silk string. I shall now take this balloon (holding it by the neck), and lay it on the table; it will not, however, remain there, but, as you will presently see, rapidly ascend to the ceiling of the lecture room; there it goes!

Another experiment—and the last I shall now perform—in illustration of this property consists in *pouring* hydrogen *upwards* from one jar into another, thus: here is a jar of hydrogen, and here another jar (a little smaller) containing nothing but air; by raising the jar of hydrogen out of the water and bringing its mouth downwards, and gently sloping it under the mouth of the jar containing air, I can thus, as it were, pour the hydrogen up into the other jar—it being a principle of hydrostatics that a light fluid must rise through a heavier one—the hydrogen rises through and displaces the air from this jar in the same manner and for the same reason as it rose through and displaced the water in the jars standing on the shelf of the pneumatic trough. The fact that the hydrogen has transferred itself into the upper jar may easily be made manifest: first, by immersing a lighted taper in the jar that was originally occupied by air, when it will (as is

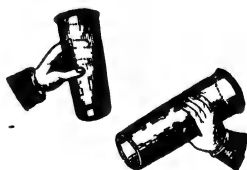


Fig.

now the case) be extinguished, and rekindled on withdrawing it through the space where you see the hydrogen burning in contact with the air, thus proving that there is hydrogen in this jar; and secondly, by immersing the lighted taper in the other jar,—the one originally occupied by hydrogen—you observe that it burns away as it did in the air previous to immersing it, thus proving that there is no hydrogen in this jar.

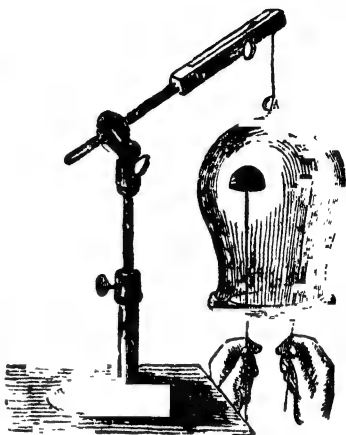


Fig. 9.

An atmosphere of hydrogen owing to its levity conducts sound so feebly as to be almost inaudible; the truth of this statement is easily proved by ringing a bell in a large jar (Fig. 9) filled with the gas, and comparing the sounds thus produced with those produced by the same means in the air only.

**Methods of Preparation.**—Hydrogen is always obtained either by the decomposition of water or of some acid.

The simplest, but at the same time the most expensive, mode of preparing hydrogen consists in decomposing water by the aid of the alkali metal potassium. When a little bit\* of potassium is thrown into water, the water

\* Care must be taken not to use too large a piece of potassium; a piece about the size of a small pea may be used with safety; if this precaution be neglected, a dangerous explosion may be the consequence. Sodium will answer equally well; and it has the advantage of cheapness.



immediately begins to decompose by exchanging its hydrogen, atom by atom, for an equivalent portion of potassium, and at the same time liberating the displaced hydrogen. The action of potassium on water is represented by a chemical equation as follows :—



that is, two molecules of water and one molecule of potassium yield two molecules of potassium hydrate (KHO) and one molecule of hydrogen—or, in other words, when water is decomposed by potassium, or sodium, half of its hydrogen is set free. Potassium, being lighter than water, will float\* when thrown into that liquid; and the hydrogen, being liberated in contact with the oxygen of the surrounding air, will be set on fire by the heat evolved by the combination of the potassium with the oxygen of the water; the heat evolved is so great as to volatilize a portion of the potassium which imparts a violet colour to the flame.

Two atoms of potassium replace 2 atoms of hydrogen; hence 1 atom of potassium is equivalent to 1 atom of hydrogen, and this fact is indicated by writing the symbol for potassium thus: K'

By wrapping the piece of potassium in blotting-paper, or in a wire-gauze spoon, and immersing it in a pneumatic trough just beneath the mouth of a cylindric jar full of water, the hydrogen gas may be collected and its properties examined.

If the cylindric glass jar be filled with infusion of purple cabbage instead of plain water, the fact of the potassium being converted into potassic hydrate (caustic potash), by its combination with the oxygen of the

\* An amalgam of potassium or of sodium may be used for greater convenience.

water, becomes evident by the change of the original purple-blue colour to green.\*

Potassium and sodium break up water at ordinary temperatures, while other metals, such as iron, require a good red heat before they will decompose it. A bar of *white-hot* iron immersed under a jar filled with water has been long known to liberate hydrogen from the water—but the quantity thus obtainable, being small, renders this method unpracticable where hydrogen is required for experimental purposes.

Another method for obtaining free hydrogen by the decomposition of water is occasionally employed. It consists in passing steam over chips of iron which are brought to a red heat in a gun-barrel or similar wrought-iron tube (see Fig 10).

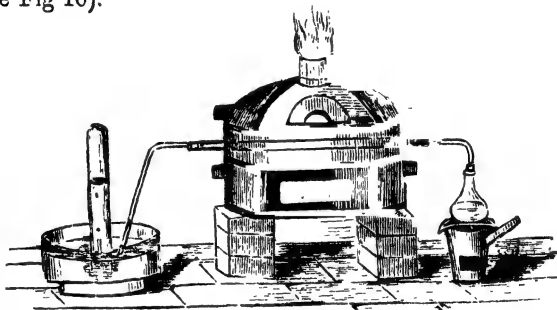
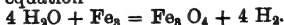


Fig. 10.

As the water-gas passes over the red-hot metal, it parts with its oxygen, which, combining with the iron, forms an oxide of iron,† while its hydrogen passes on, and may be

\* Such a change of colour is characteristic of the alkali potassic hydrate, see p. 91.

† The oxide produced in this case is called the black oxide of iron, also the magnetic oxide of iron. The reaction which takes place is represented by the equation—



Charcoal may be substituted for the iron chips, when the equation becomes  $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ .

collected in jars over the pneumatic trough. The property of decomposing water which is possessed by red-hot iron may be proved in a more simple manner (than by using the complicated apparatus represented in Fig. 10), by plunging a bar of red-hot iron into the pneumatic trough directly under the mouth of a gas jar filled with water, when it will be seen that bubbles ascend and displace some of the water in the jar. These bubbles are composed of hydrogen mixed with air.

The method most generally employed for preparing hydrogen may be described as follows:—Into a Wolfe's or two-necked bottle\* (see Fig. 11) some granulated zinc† is introduced. The necks of the bottle must now be closed by corks, one of which carries a bent

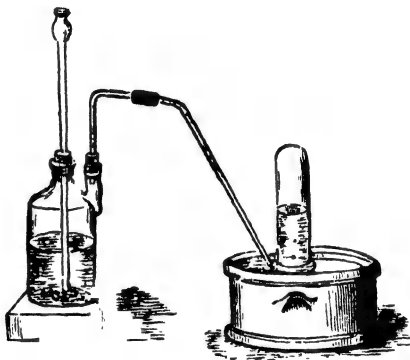


Fig. 11.

delivery tube, and the other is traversed by a thistle funnel reaching to within about half an inch of the bottom of the bottle. As much distilled water as will cover the zinc and the lower end of the long funnel must then be poured into the bottle through the funnel. The next thing is to ascertain whether the joints closed by the

\* A wide-mouth bottle, fitted with a large cork in which two holes are bored, will answer quite as well.

† The zinc may be granulated by melting it in an iron ladle, and then pouring it into water.

corks be air-tight or not. This may be proved by blowing through the funnel, when, if a leak exists, you will hear a hissing sound caused by the escape of the air within; or by placing your warm hands on the sides of the bottle, which causes the enclosed air to expand, thereby increasing the pressure on the surface of the water; consequently a column of water will rise in the funnel-tube; if on removing your hands the column of water be observed to fall gradually to its original level, you may be satisfied that the corks are staunch; if the corks be found leaky, they must be staunched either by painting with sealing-wax varnish, or by covering them with a plaster of linseed meal (or with plaster of Paris), before proceeding further with the experiment. Such precautions must be attended to in the preparation of all gases.

Having proved that our apparatus is air-tight the experiment may be proceeded with by pouring a few drops of hydrogen sulphate\* into the bottle through the funnel, and then gently shaking the bottle, when brisk effervescence commences, produced by the escape of the hydrogen gas through the liquid.  $H_2SO_4 + Zn = ZnSO_4 + H_2$ . By occasionally adding a few drops of hydrogen sulphate (sulphuric acid) a continual stream of bubbles of gas is kept up. Care must be taken not to add too much acid at a time, otherwise the action may become so violent as to cause the contents of the bottle to froth over. Should the action at any time appear unduly brisk, it is better to add a little more water, which will dilute the acid solution and thereby quiet the action, as well as prevent the zinc sulphate from forming an insoluble film on the surface of the zinc

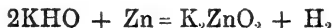
\* The hydrogen sulphate may be replaced by hydrogen chloride, in which case no water is necessary, and the reaction is represented thus:  $-2HCl + Zn = ZnCl_2 + H_2$ . The zinc may be replaced by iron, when the formula becomes  $2HCl + Fe = FeCl_2 + H_2$ .

(zinc sulphate being insoluble in the concentrated acid), thus protecting it from the further action of the hydrogen sulphate. Filling as many jars with the gas which comes over at first as are about equal to twice the capacity of the generating bottle, we reject this quantity in consequence of its being mixed with air,\* and then collect three or four jars of pure hydrogen. The jars should not be filled completely, as in consequence of the levity of the hydrogen gas they might turn over with the slightest gust of wind; it is sufficient to fill them so that the level of the water inside the jar shall be the same as that in the trough.

When gaseous hydrochloric acid is heated in presence of the metal sodium, the latter combines with the chlorine, liberating hydrogen, thus :—



When a solution of potassium hydrate (caustic potash) is heated in contact with metallic zinc or iron, hydrogen is evolved.



Hydrogen is also evolved from almost all aqueous solutions of ammonia† when brought into contact with zinc (best at a temperature of about 40° C.). From a mixture of iron, zinc, and a solution of sal ammoniac hydrogen is freely evolved.

**Quantitative Calculations.**—It can be proved experimentally (by performing the necessary weighings, &c.) that 2 parts by weight of hydrogen are liberated when 65 parts by weight of zinc are dissolved in hydrogen sulphate, and

\* A mixture of hydrogen and air produces a dangerous explosion when brought into contact with a lighted taper.

that if the sulphate of zinc which remains in the bottle in solution be separated from the water and dried, it will be found to yield 161 parts by weight. Whatever excess of acid may have been used remains in the bottle mixed with the water. These experimental facts are represented in a concise and intelligible form by the following equation :—

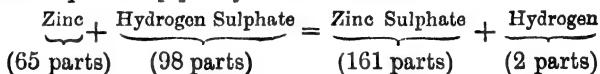


Now, according to our Table of atomic weights,  $\text{Zn}=65$ ,  $\text{H}=1$ ,  $\text{S}=32$ , and  $\text{O}=16$ .

$$\therefore \text{H}_2 \text{SO}_4 = (1 \times 2) + (32 \times 1) + (16 \times 4) = 98,$$

$$\text{and } \text{Zn SO}_4 = (65 \times 1) + (32 \times 1) + (16 \times 4) = 161.$$

Hence equation [2] may be written thus :—



So the equation states (in a concise manner) that 65 parts by weight of zinc and 98 parts by weight of hydrogen sulphate yield 161 parts by weight of zinc sulphate and 2 parts by weight of hydrogen.

Two atoms of hydrogen are replaced by 1 atom of zinc ; hence 1 atom of zinc is equivalent to 2 atoms of hydrogen. Zinc is therefore a *dyad* element.

If the atomic proportions be taken in grams, then the equation further asserts that every 65 grams of zinc displace 2 grams of hydrogen from every 98 grams of hydrogen sulphate brought in contact with it under the circumstances I have described to you. It will thus be an easy task to calculate the quantities of zinc and hydrogen sulphate required to produce a given quantity of hydrogen. For example—

Let it be required to calculate how much zinc and hydrogen sulphate are required to produce 25 grams of hydrogen.

As 65 grams of zinc are required for 2 grams of hydrogen,

$$\begin{array}{ccccccc} \frac{65}{2} & & & & & 1 \text{ gram} & \\ & \text{''} & & \text{''} & & & \\ \therefore \frac{65}{2} \times 25 & & & & & 25 \text{ grams} & \end{array}$$

Ans. Quantity of zinc =  $\frac{65}{2} \times 25 = 812.5$  grams.

Or by simple proportion thus:—

$$\begin{array}{ccccccc} \text{Hydrogen} & & \text{Hydrogen} & & \text{Zinc} & & \text{Zinc} \\ \hline (2 \text{ grams}) & : & (25 \text{ grams}) & :: & (65 \text{ grams}) & : & (x \text{ grams}) \\ & & & & \therefore x = \frac{65 \times 25}{2} = 812.5 \text{ grams of zinc.} \end{array}$$

The quantity of hydrogen sulphate is determined as follows:—

As 98 grams of hydrogen sulphate yield 2 grams of hydrogen,

$$\begin{array}{ccccccc} \frac{98}{2} & & & & & 1 \text{ gram} & \\ & \text{''} & & \text{''} & & & \\ \therefore \frac{98}{2} \times 25 & & & & & 25 \text{ grams} & \end{array}$$

Ans. Quantity of hydrogen sulphate =  $\frac{98}{2} \times 25 = 1225$  grams.

Or by simple proportion thus:—

$$\begin{array}{ccccccc} \text{Hydrogen} & & \text{Hydrogen} & & \text{Hydr. Sulph.} & & \text{Hydr. Sulph.} \\ \hline (2 \text{ grams}) & : & (25 \text{ grams}) & :: & (98 \text{ grams}) & : & (x \text{ grams}) \\ & & & & \therefore x = \frac{98}{2} \times 25 = 1225 \text{ grams.} \end{array}$$

### THE HALOGENS.

#### Chlorine—Bromine, Iodine and (Fluorine).

Of the other *monad* elements chlorine, bromine, iodine, and fluorine are next in importance. The compounds which these elements form with the metals sodium, potassium, and magnesium, so closely resemble common

sea-salt (sodium, chloride) that Berzelius gave the title of *halogen\** to the group.

These elements possess the common property of combining with hydrogen in the proportion of atom to atom, producing by their combination, in each case, a strongly acid body which is gaseous and soluble in water.

HCl = hydrochloric acid.

HBr = hydrobromic acid.

HI = hydriodic acid.

HF = hydrofluoric acid.

These are the halogen acids; they are also frequently termed *hydracids*, in contradistinction to the so-called *oxyacids*, or acids containing oxygen, like nitric ( $\text{HNO}_3$ ) and sulphuric ( $\text{H}_2\text{SO}_4$ ) acids.

Fluorine has resisted most attempts at isolation up to the present time.† The other three members of the group are well known, and present marked *gradational differences* in properties. Chlorine is a *gas* while bromine is *liquid* and iodine *solid* at ordinary temperatures and pressures. The atomic weight and vapour-density of bromine are intermediate (just the mean) between those of chlorine and iodine.

$$\left. \begin{array}{l} \text{Cl} = 35.5 \\ \text{Br} = 80 \\ \text{I} = 127 \end{array} \right\} 80.8 = \text{mean.}$$

Bromine is, again, intermediate in chemical activity; for chlorine expels bromine from bromides, while bromine in turn expels iodine from iodides.

**Methods of Preparation.**—The common source of these three elements is sea-water. Chlorine is obtained from common salt ( $\text{NaCl}$ ), bromine from the magnesium

\* From ἅλς sea-salt, γεννάω produce.

† Its hydrogen compound is, however, well known, and is used in the arts for etching on glass, being obtained from Fluor-Spar by the action of sulphuric acid. [ $\text{H}_2\text{SO}_4 + \text{CaF}_2 = \text{CaSO}_4 + 2\text{HF}$ .]



bromide ( $\text{Mg Br}_2$ ) present in sea-water, and iodine from *kelp*, the ashes of certain seaweeds (containing  $\text{NaI}$ ) growing on the coasts of Scotland, Ireland and France.

Preparatory to the preparation of chlorine, *hydrochloric acid* ( $\text{HCl}$ ) is first obtained, by the action of sulphuric acid on common salt

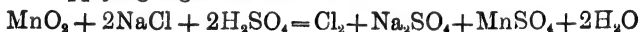


Sodium di-sulphate (called *salt cake*) is also produced.

Then some of the chlorine of the hydrochloric acid is liberated by the action of manganese dioxide—a substance which we use in the preparation of oxygen—while chloride of manganese and water are formed.



A more convenient method of preparing chlorine for experimental purposes in a laboratory consists in mixing the materials used for preparing hydrochloric acid with a sufficiency of the manganese ( $\text{MnO}_2$ ) in a large glass flask and applying a gentle heat.



The gas should be collected over hot water or by displacement of air; it cannot be collected over mercury, as it enters into rapid combination with that metal.

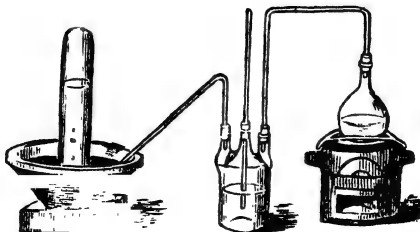


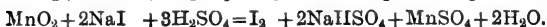
Fig 12.  
Collecting chlorine over hot water.

By this process the hydrochloric acid from which the chlorine is liberated is evolved in the same vessel in which it is, at the same time, acted on by the manganese. It is usual to employ a larger proportion of sulphuric acid than represented in last equation, so that acid sodium sulphate may be left in the glass flask, which can then be easily washed out.



The mixture most generally used consists of one part manganese, 1 part salt, and 2 parts strong acid previously mixed with twice its volume of water and cooled.

Exactly similar reactions occur in the preparation of bromine and iodine from bromides and iodides respectively\*—



**Chlorine** is a yellowish-green gas with a suffocating odour which, when diluted largely with air, somewhat resembles that of seaweed; it should not be inhaled, as it produces severe irritation of the bronchial passages, and even death. The dry gas is condensed into an oily-looking liquid when cooled under a pressure of five or six atmospheres. Chlorine has a great affinity for hydrogen, and equal volumes are exploded (producing fumes of hydrochloric acid) on exposure to heat, or even to sunlight or to the light of a magnesium taper. The bleaching action of chlorine, which renders it so valuable in the arts of bleaching cotton, linen and paper goods, is mainly due to its power of combining with hydrogen and the consequent liberation of oxygen, which in the nascent state readily combines with colouring matters, and thus bleaches them. Water dissolves twice its volume of

\* These processes are now in full operation on the Lecture Table, and you can recognise the presence of Iodine and Bromine from their colours—*violet* and *red*, respectively.

chlorine, and chlorine water is frequently used for bleaching as well as for disinfecting purposes. This solution cannot be long kept, for on exposure to sunlight (even to diffused daylight) the chlorine displaces oxygen and combines with hydrogen, thus producing (in solution) hydrochloric acid and dissolved oxygen.



It is this liberated oxygen which is the real bleaching agent.

Chlorine is therefore indirectly an oxydising agent owing to the power it has of robbing certain oxidised bodies of their hydrogen.

For storing chlorine for use in the art of bleaching, it is usual to conduct the gas into slaked lime with which it partly combines to form the well-known bleaching powder (popularly, though wrongly, called chloride of lime); its composition is represented by the formula  $\text{CaCl}_2 + \text{Ca}(\text{ClO})_2$ ; and it readily gives off chlorine gas when treated with a dilute acid.

Chlorine forms but one compound with hydrogen, namely, hydrochloric acid gas ( $\text{HCl}$ ), the solution of which in water is sometimes called muriatic acid, on account of its being prepared from sea salt (*muria*).

A candle burns in chlorine gas, the hydrogen of the fat combining with the chlorine to form hydric chloride, while carbon is set free as a black smoke. Turpentine and other hydrocarbons also readily burn in chlorine by a similar action.

Chlorine combines readily with most of the metals; powdered antimony and gold leaf take fire spontaneously in dry chlorine gas.

*Names and Formulæ of Familiar Chlorides.*

Hydrogen Chloride	= $\text{HCl}$ (Muriatic acid).
Argentichloride	= $\text{AgCl}$ (Horn Silver)

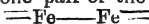
Sodium Chloride	= NaCl (Salt)
Potassium Chloride	= KCl
Plumbic Chloride	= PbCl <sub>2</sub>
Mercurous Chloride	= Hg <sub>2</sub> Cl <sub>2</sub> (Calomel)
Mercuric Chloride	= HgCl <sub>2</sub> (Corrosive Sublimato)
Zinc Chloride	= ZnCl <sub>2</sub>
Cuprous Chloride	= Cu <sub>2</sub> Cl <sub>2</sub>
Cupric Chloride	= CuCl <sub>2</sub>
Stannous Chloride	= SnCl <sub>2</sub> (Dyer's Salt)
Stannic Chloride	= SnCl <sub>4</sub>
Ferrous Chloride	= FeCl <sub>2</sub>
* Ferric Chloride	= Fe <sub>2</sub> Cl <sub>6</sub>
Aluminic Chloride	= Al <sub>2</sub> Cl <sub>6</sub>
Chromic Chloride	= Cr <sub>2</sub> Cl <sub>6</sub>
Antimonous Chloride	= SbCl <sub>3</sub>
Antimonic Chloride	= SbCl <sub>5</sub>
Aurous Chloride	= AuCl
Auric Chloride	= AuCl <sub>3</sub>
Ammonium Chloride	= NH <sub>4</sub> Cl
Platinous Chloride	= PtCl <sub>2</sub>
Platinic Chloride	= PtCl <sub>4</sub>

*Insoluble Chlorides.*—With three exceptions, the chlorides of all the metals are soluble in water; the exceptions are silver (AgCl), mercurous (Hg<sub>2</sub>Cl<sub>2</sub>), and lead (PbCl<sub>2</sub>) chlorides; these are therefore at once distinguished from all other chlorides by their *insolubility* in water, and they are distinguished from each other by their behaviour with ammonium hydrate (NH<sub>4</sub>HO) which reagent dissolves the first, blackens the second, and leaves the third unchanged.

#### Halogens with Hydrogen and Oxygen :—

In the following table we have a list of the known acids formed by the Halogens by combining with Hydrogen and Oxygen :—

\* The apparent tri-atomicity of iron in ferric compounds is explained by the combination of one pair of the *tetrad* bonds of the double iron atom.



(I)	(II)	(III)	(IV)	(V)
HF	—	—	—	—
HCl	HClO	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>
HBr	HBrO	—	HBrO <sub>3</sub>	HBrO <sub>4</sub>
HI	—	—	HIO <sub>3</sub>	HIO <sub>4</sub>

(The blanks indicate compounds not yet prepared.)

Taking the chlorine compounds alone as representing a complete series, we may learn to distinguish the following series of compounds as oxides or oxy-acids of chlorine in which the chlorine atom appears to change its valency from *one* to *seven*.

*Oxides* (with water forming) *Oxy-acids*.

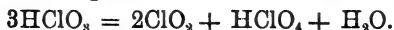
Hypochlorous anhydride	} Cl <sub>2</sub> O	Hypochlorous acid	} HClO
Chlorous anhydride	} Cl <sub>2</sub> O <sub>3</sub>	Chlorous acid	} HClO <sub>2</sub>
Chlorine peroxide	} ClO <sub>2</sub>	No corresponding single acid formed	} HClO <sub>3</sub> + HClO <sub>4</sub>
No correspon- ding oxides	} —	Chloric acid	} HClO <sub>4</sub>
	} —	Perchloric acid	} HClO <sub>4</sub>

The oxides Cl<sub>2</sub>O<sub>6</sub> and Cl<sub>2</sub>O<sub>7</sub>, corresponding to chloric and perchloric acids have not yet been separately prepared, while ClO<sub>2</sub> (or Cl<sub>2</sub>O<sub>4</sub>), the peroxide, resembles nitrogen peroxide, forming with water mixed acids (HClO<sub>3</sub>+HClO<sub>4</sub>) and with bases a mixture of chlorates and chlorites.

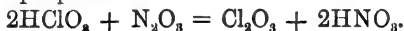
*Chlorine peroxide*, which is a dangerously explosive substance, is evolved as a heavy, dark yellowish-red, gas, smelling like a mixture of burnt sugar and chlorine, when *potassium chlorate* is treated with concentrated sulphuric acid.\* The gas often explodes on exposure to light, being resolved into elementary chlorine and oxygen. The

\* This experiment is best avoided, unless the student has learnt how to manipulate from a competent teacher. The same remark applies to the other oxides of chlorine.

sulphuric acid at first liberates chloric acid from the chlorate, which, owing to its instability, is further resolved into the peroxide, perchloric acid and water, thus :—



*Chlorous anhydride*  $\text{Cl}_2\text{O}_3$ , is a yellow-green gas with a very pungent smell, even more irritating to the respiratory organs than chlorine; it is dangerous to breathe it. It may be prepared on a small scale by bringing about the slow dioxidation of chloric acid; nitrogen trioxide serves this purpose :—



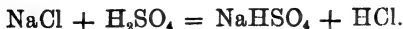
A mixture of potassium chlorate with arsenious anhydride and nitric acid in suitable proportions also serves to obtain a supply of this gas. The nitric acid liberates  $\text{HClO}_3$ , which is then reduced by the arsenious oxide.\*

*Hypochlorous anhydride*,  $\text{Cl}_2\text{O}$ , is a yellow-coloured gas having a smell resembling that of chlorine; it is also a dangerous gas to prepare owing to its tendency to explode violently. It may be prepared by passing dry chlorine gas over dried precipitated oxide of mercury (kept cool), the reaction being

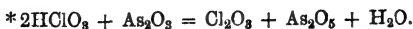


white mercuric oxychloride being the only other product.

**Hydrochloric Acid.**—This gaseous body, already mentioned as forming the only compound of chlorine and hydrogen, is readily evolved when sulphuric acid is made to act on, almost, any chloride—fused common salt ( $\text{NaCl}$ ) being generally employed, in the following proportions when glass apparatus is used in its preparation :—



The acid sodium sulphate  $\text{NaHSO}_4$  thus formed is



more easily washed out of a glass flask or retort than the normal sulphate, or salt cake ( $\text{Na}_2\text{SO}_4$ ). An apparatus similar to that used in the preparation of chlorine answers the purpose. On the commercial scale large iron cylinders are employed, and the gas is condensed in brick flues packed with moistened coke.

Hydrochloric acid is a transparent gas which fumes readily in moist air. It possesses an intensely acid taste; it irritates the eyes and membranes of the nose and throat. It has a peculiar pungent odour. It is extremely soluble in water. When a jar of the gas is opened under water, the latter rushes in with great violence, filling the jar. Water at  $15^\circ \text{C}$ . absorbs more than 450 times its own bulk of the gas. Hydrogen chloride, whether free or in solution, is decomposed by an alkali metal with evolution of hydrogen gas—occupying half the original volume of  $\text{HCl}$ . Hence *two volumes* of hydric chloride contain one volume of hydrogen—the other volume being chlorine.

The gas extinguishes a lighted taper, nor does it take fire itself.

A solution of hydrochloric acid gas is decomposed by electrolysis, giving equal volumes of hydrogen and chlorine. Its composition may also be ascertained by synthesis by exploding equal volumes of hydrogen and chlorine in a suitable tube.

The aqueous solution is a very useful reagent, and is largely employed in Chemical Laboratories for dissolving metals, &c.

Bromine, Iodine and Fluorine being comparatively rare elements, it is not thought advisable to introduce into the present elementary course a *separate* description of each element and its compounds. Bromides and Iodides are used only in medicine and photography.

## CHAPTER XII.

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### OXYGEN.

$O'' = 16$  ; Density = 16.

**History.**—Oxygen was discovered in the year 1774\* by the English chemist Priestley, and in 1775 by the Swedish chemist Scheele, who it is said was unaware of its previous discovery in England. Priestley, supposing it to be air deprived of the imaginary substance named ‘phlogiston’ by Stahl, called it ‘dephlogisticated air.’ Scheele called it ‘vital air,’ from its property of supporting animal life. Lavoisier gave it its present name oxygen from *ὄξυς* (*oxus*) acid, and *γεννάω* (*gennao*) I produce—believing it to be a necessary constituent of all acids.†

**Occurrence.**—This is the most widely-distributed substance in Nature ; it occurs to the extent of more than one-third of all the rock-materials composing the earth’s crust, and (as I shall presently prove) constitutes eight-ninths of the weight of the water, and one-fifth of the bulk of the atmosphere, which surround the world on which we live. Fully one-half of the matter of living plants and animals is also composed of oxygen.

**Properties.**—Here is a jar of oxygen. You perceive it has no colour—it is as invisible as air. Take the jar in your hands, examine the gas with your nose, and satisfy

\*The birth of Chemistry may be said to date from the discovery of oxygen—i.e. from 1st August, 1774.

† Although most acids contain oxygen, yet we *now* know of many in which oxygen does not exist at all—the halogen acids for example.



yourselves that it has no smell. We can dissolve some of it in water : 100 cubic inches of water at  $0^{\circ}\text{C}$ . are capable of dissolving 4 cubic inches of this gas. Here is some water containing oxygen in solution ; drink a little of it, and notice that it has no taste. It is of great importance to fish and other breathing inhabitants of seas, rivers, &c., that their waters are capable of dissolving oxygen—such animals being dependent on the *dissolved oxygen* for their ‘vital air.’ Fishes die if put into water from which the dissolved oxygen has been removed. You must remember that the oxygen which water contains in solution is not any portion of the oxygen of which water is partly composed ; the *dissolved oxygen* can be removed from it, without in the least interfering with its constituent oxygen ; the dissolved oxygen, being merely mechanically mixed with the water, is removed by boiling.

With the apparent exception of fluorine,\* oxygen is capable of combining with every one of the elements. Its combination with many of the elements is attended with the phenomena of combustion : for example :—

If I insert this piece of red-hot charcoal (*i.e.* carbon) into a jar of oxygen, it will burst into a brilliant *glow*. I now withdraw the piece of charcoal, and almost quenching it I again plunge it into the oxygen : you observe that it is rekindled. I may repeat this a great number of times, in fact until all the oxygen has combined with the carbon of the charcoal, and thus formed the compound called *carbonic anhydride*,  $\text{CO}_2$ . Instead of a piece of charcoal I may use a chip of wood, which having first

\* The conditions necessary to effect the combination of oxygen and fluorine may yet be discovered ; hence we cannot say absolutely that oxygen will not unite with fluorine.

lighted I blow out, leaving it glowing red. As I plunge this chip\* into another jar of oxygen, you notice that it bursts quickly into *flame* and burns brilliantly. For the chip of wood I may substitute a candle or taper with similar results.

Into this curious-looking spoon (Fig. 13), which we call a deflagrating spoon (from the Latin *deflagro*, I burn), I put a small piece of sulphur (or brimstone), and ignite it in the lamp; you observe it burns slowly and with but little light. Now I plunge the burning sulphur into a large jar or bottle full of oxygen (Fig. 14): there, you see, it bursts into a fuller state of combustion with a rich



Fig. 13.

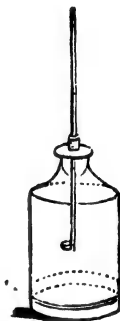


Fig. 14.

violet-blue flame. The product of the combustion of sulphur in oxygen is (an acid oxide of sulphur) called sulphurous anhydride,  $\text{SO}_2$ .

Now let us try a similar experiment with phosphorus. Taking a small piece about the size of a pea, I first dry it between two folds of blotting-paper, and then, igniting it

\* Chips of cedar-wood are best-suited for this experiment.

by touching it with a hot wire, I introduce it into a fresh jar or globe filled with oxygen (Fig. 15) and you observe the effect: the phosphorus and oxygen rapidly combine, producing a brilliant light and considerable heat. When this experiment is performed in a dark room, the light becomes so intense that you can scarcely look at it. The product of the combustion in this case is a snow-like solid, called phosphoric anhydride,  $P_2O_5$ .

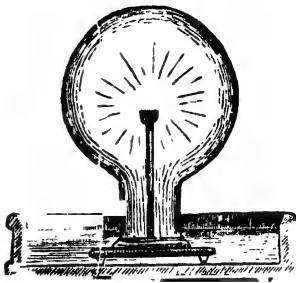


Fig. 15.

A more beautiful experiment than any of the preceding ones may be made by burning iron wire in oxygen. A piece of watch-spring or a coil of iron or steel wire, such as harpsichord wire, is generally used for this purpose. Having formed the wire into a spiral by coiling it on a thick glass rod, I dip one end of the coil into melted sulphur, and fasten the other end into a cork, which fits a large glass deflagrating jar containing oxygen, and standing in a good-sized tray of water. Having lighted the sulphur on the tip of the wire, I remove the glass stopper from the jar, and insert the coil of wire, lowering it till I can close the mouth of the jar with the cork, which is attached to the spiral (Fig. 16).

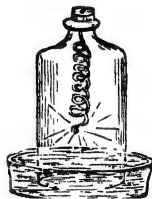


Fig. 16.

The burning sulphur produces heat sufficient to *start* the combustion of the oxygen with the wire; once begun, however, sufficient—and much more than sufficient—heat to continue the act of combination is evolved, during the

union of the iron with the oxygen. The oxidation of the iron proceeds with rapid combustion, yielding a light of dazzling splendour. That the oxygen is really absorbed by the iron is evidenced by the water rising in the jar to replace it. That great heat is evolved by the combination of the iron and oxygen is manifested by the fact that the oxide of iron, which is formed, drops down in a molten state, and falling on the stoneware tray, burns into its bottom: to prevent injury to the tray from this cause it is usual to have a layer of sand on the bottom of the tray. The product of the combustion in this case is the black (or magnetic) oxide of iron, the formula of which is  $\text{Fe}_3\text{O}_4$ .

From these experiments we learn that a very remarkable property of oxygen is its *capability of supporting and increasing combustion*.

From the same experiments we also learn that the phenomena of combustion, in oxygen at least, are due to the act of combination, by which heat is always and light very often developed. The phenomena of combustion in oxygen and in air are essentially the same in nature, differing only in degree. When charcoal, wood, sulphur and phosphorus, &c., are burned in air, the products formed are exactly the same as when these substances are burned in oxygen; but the *rapidity* with which combustion takes place in pure oxygen causes *more intense* heat and light to be evolved than is the case when combustion takes place in air only. Though the *intensity of the heat* may differ, still the *same substance* always evolves the *same quantity of heat*, whether burned in air or pure oxygen: thus, the quantity of heat developed by the combustion of 12 grams of charcoal in air is exactly equal to the quantity of heat evolved by the combustion of 12 grams of charcoal in pure oxygen. The evolution of a

definite quantity of heat by the burning of the 12 grams of carbon in oxygen is, as it were, compressed into a shorter period of time than the evolution of the *same quantity* by the slower process of burning 12 grams of carbon in atmospheric air: hence the former is more intense than the latter; in each case, however, the same compound ( $\text{CO}_2$ ) and the same weight of it is formed; and the amount of heat produced in either case would melt exactly the same quantity of ice.

Oxygen possesses the important property of supporting the respiration of animals; it is by virtue of its presence in a *free state* in the air we breathe that our life is maintained; the pure gas, however, has too stimulating an effect on our system; and hence it is, wisely, diluted for us in the atmosphere by an admixture of a large share of nitrogen. That the oxygen of the atmosphere is necessary for life is easily proved by introducing a small animal, such as a rat or mouse, into a jar of air deprived of its oxygen. If this be done, the animal will die in a few moments. I shall have more to say on the subject of respiration when we come to consider the chemistry of the atmosphere.

Oxygen is heavier than air, in the proportion of 1.1056:1. One liter weighs 16 *criths*, at the normal temperature and pressure.

So recently as December, 1877, MM. Pictet and Chailletet succeeded by the combined application of intense cold and great pressure in condensing oxygen and nitrogen into the liquid condition.

**Methods of Preparation.**—Oxygen is usually prepared from some metallic oxide or salt containing it, merely by the application of *heat*,—the most useful agent the chemist can employ.

It was first prepared by Dr. Priestley from the red oxide of mercury,  $\text{HgO}$ . To obtain oxygen by this method, I take about 1 gram of this red powder (*i.e.* mercuric oxide), and introducing it into a *hard* glass tube to which is fitted a cork carrying a bent glass delivery tube, I apply the flame of a lamp to its bottom; when a certain temperature is reached, the red powder splits up into its two components, mercury and oxygen; the mercury sublimes into the upper part of the tube, and the oxygen, being a gas, passes off by the eduction tube.

The decomposition of the mercuric oxide by heat is represented in the form of an equation, thus—



which simply states that 216 parts by weight of the red oxide of mercury yield 200 of metallic mercury and 16 of oxygen gas. Mercuric oxide being an expensive material other methods are now employed.

A more suitable material—and the one from which oxygen is generally prepared—is the salt called potassium chlorate, a molecule of which is represented by the formula  $\text{KClO}_3$ .

To obtain oxygen from this salt we may use the apparatus represented in Fig. 17, into which is introduced some chlorate of potassium which has been previously dried and crushed in a mortar. When heat is applied

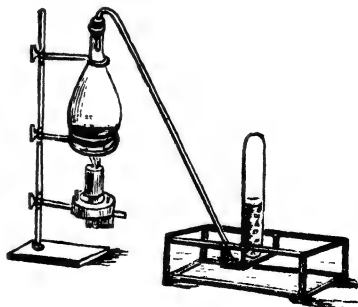


Fig. 17.

\* Molecularly expressed this equation becomes  $2 \text{HgO} = 2 \text{Hg} + \text{O}_2$ .

to the flask the chlorate first melts into a clear liquid, and after a little time oxygen gas begins to bubble through it: by continuing the heat sufficiently, the entire of the oxygen of the potassium chlorate may be liberated from its combination with the potassium and chlorine, leaving only *potassium chloride*,  $\text{KCl}$ , in the flask.

The decomposition which the potassium chlorate undergoes, by the application of sufficient heat, is represented by the equation—



The temperature required to liberate the *entire* of the oxygen by this process becomes so high towards the end as to endanger the bottom of the flask. This inconvenience, however, is quite removed by mixing with the chlorate about one-fourth its weight of the peroxide of manganese  $\text{MnO}_2$  (commonly called manganese) or of the black oxide of copper  $\text{CuO}$  or of ferric oxide  $\text{Fe}_2\text{O}_3$  (iron rust); the manganese, being the cheapest, is usually employed.

When the potassium chlorate is mixed with one-fourth its weight of manganic peroxide ( $\text{MnO}_2$ ) the oxygen is given off at a much lower temperature than that required for its liberation from the chlorate alone;\* the oxygen, however, is not so pure, it being generally accompanied by traces of chlorine gas. This is, however, got rid of by passing the oxygen gas through cold water contained in a wash bottle before collecting it in the bag.

A copper retort is usually employed for preparing oxygen when required in large quantities. The accompanying sketch, Fig. 18, represents the necessary apparatus.

\* The mode of action of the Manganese oxide is not well understood; it goes by the name of *Catalysis*.

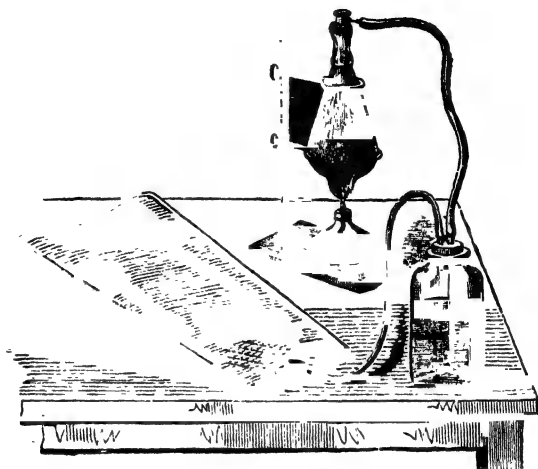


Fig. 18.

## APPARATUS FOR PREPARING AND COLLECTING OXYGEN.

**Ozone** (from  $\delta\acute{\xi}\omega$ , I smell) is a molecular modification of oxygen gas, possessing a *peculiar smell*. It is thought to be oxygen in an altered state, and is consequently frequently called *allotropic*\* oxygen—*i.e.* another form of oxygen. Ozone is formed when a series of electric sparks are passed through ordinary oxygen or air, which, at the same time, undergoes a condensation of volume,—3 volumes of ordinary oxygen condensing into 2 volumes of ozone. This allotropic oxygen is characterized by great chemical activity, which is manifested by its decomposing potassium iodide, by its corroding cork, india-rubber and other organic substances, by its bleaching indigo and

\* From  $\acute{\alpha}\lambda\lambda\omicron\varsigma$  (*allos*) another, and  $\tau\rho\omicron\pi\omicron\varsigma$  (*tropos*) form.



paper stained with sulphide of lead,\* and by a variety of other oxidating actions.

The peculiar smell usually perceived during the working of an Electric Machine is thought to be due to the formation of ozone, for when *ozone-paper* (*i.e.* starch paper dipped in a solution of potassium iodide) is held in front of a point attached to the conductor of the machine, the paper turns blue, in consequence of the formation of the well-known blue compound iodide of starch.†

The study of the properties of ozone is chiefly interesting in consequence of a belief that it exists in the atmosphere, and that it there performs the important duty of oxidizing the decaying organic matter arising from animal and vegetable exhalations.

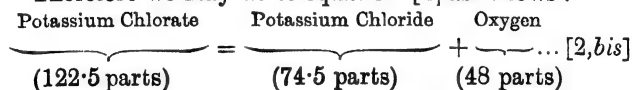
**Quantitative Calculations:**—By referring to Table D (page 43) we find  $K = 39$ ,  $Cl = 35.5$ ,  $O = 16$ .

$$\therefore KClO_3 = (39 \times 1) + (35.5 \times 1) + (16 \times 3) = 39 + 35.5 + 48 = 122.5.$$

Hence the molecular weight of potassium chlorate = 122.5.

By addition we also find that  $KCl = 74.5$ , and since  $O = 16$ ,  $O_3$  must be equal to 48.

Therefore we may write equation [2] as follows:—



This equation simply states that when sufficient heat is applied to potassium chlorate, every 122.5 parts (*by weight*)

\* This is due to the conversion of the black sulphide  $PbS$  by oxidation into white sulphate of lead  $PbSO_4$ .

† Such action is characteristic of ozone; nitrous and nitric acids, however, produce the same change of colour.

of the chlorate yield 74·5 parts of potassium chloride and 48 parts of oxygen gas. If the atomic proportions of the elements be taken in grams, then equation [2] further asserts that every 122·5 grams of potassium chlorate *are capable of yielding* 74·5 grams of chloride of potassium and 48 grams of oxygen.

Hence we can calculate the weight of oxygen which can be obtained from any given weight of potassium chlorate; or, conversely, the weight of potassium chlorate required to produce a given weight of oxygen. Thus, for example:—

Let it be required to calculate the weight of oxygen which can be obtained from one kilogram of potassium chlorate.

Since 122·5 grams of chlorate yield 48 grams of oxygen,

$$1 \text{ gram} \quad ,, \quad \text{yields} \quad \frac{48}{122\cdot5} \quad ,, \quad ,,$$

$$\therefore 1 \text{ kilogram (= 1000 grams)} \quad ,, \quad \frac{48}{122\cdot5} \times 1000 \quad ,, \quad ,,$$

$$\text{Ans. Quantity of oxygen} = \frac{48}{122\cdot5} \times 1000 = 391\cdot83 \text{ grams.}$$

Conversely, how much chlorate of potassium must be used to obtain 1 kilogram of oxygen?

Since 48 grams oxygen require 122·5 grams of chlorate,

$$1 \text{ gram} \quad ,, \quad \text{requires} \quad \frac{122\cdot5}{48} \quad ,, \quad ,,$$

$$\therefore 1 \text{ kilogram (= 1000 grams)} \quad ,, \quad \frac{122\cdot5}{48} \times 1000 \quad ,, \quad ,,$$

$$\text{Ans. Quantity of chlorate} = \frac{122\cdot5}{48} \times 1000 \therefore 2552 \text{ grams.}$$

**Other Methods of Preparation:—**When oxygen is required in large quantities, it is more cheaply prepared by exposing the mineral *pyrolusite* (another name for manganese peroxide)  $\text{MnO}_2$ , to a strong red heat in an iron retort (Fig. 19). The manganese refuses, no matter how high the temperature be raised, to give off more than *one-third* of its oxygen. After all the oxygen that can be obtained is set free, there is found in the retort another oxide of manganese, the formula of which is  $\text{Mn}_3\text{O}_4$ . Hence the decomposition of pyrolusite by heat may be represented thus:—

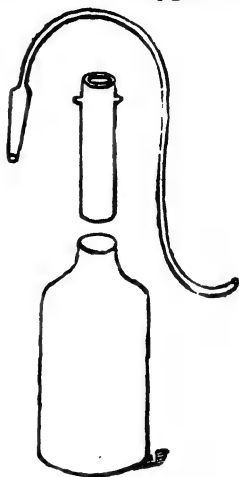
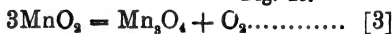


Fig. 19.



In Table D (page 43) we find  $\text{Mn} = 55$ , and  $\text{O} = 16$ ,

$$\therefore \text{MnO}_2 = 55 + 32 = 87$$

$$\text{and } 3\text{MnO}_2 = 3 \times 87 = 261.$$

We thus find that 261 parts by weight of manganese peroxide are, when sufficiently heated, capable of yielding 32 parts ( $= \text{O}_2$ ) of oxygen. Hence from every 261 grams of the manganese oxide used in preparing oxygen by this method 32 grams of oxygen may be obtained.

If it be required to calculate the quantity of oxygen which can be obtained from a given quantity of manganese (pyrolusite); or, conversely, if we wish to know how much manganese oxide is required to produce a given quantity of oxygen, we can perform the necessary calculations, as follows:—

*e.g.* Let it be required to find how much oxygen can be prepared from half a kilogram of pyrolusite.

Since 261 grams of manganese yield 32 grams of oxygen,

1 gram „ „ will yield  $\frac{32}{261}$  „ „

$\therefore \frac{1}{2}$  kilogram (= 500 grams) „  $\frac{32}{261} \times 500$  „ „

*Ans.*—Quantity of oxygen =  $\frac{32}{261} \times 500 = 61.3$  grams.

Or the problem may be solved by simple proportion, thus:—

$$\begin{array}{ccccccc} \text{Manganese} & & \text{Manganese} & & \text{Oxygen} & & \text{Oxygen} \\ \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} \\ (261 \text{ grams}) & : & (500 \text{ grams}) & :: & (32 \text{ grams}) & : & (x \text{ grams}) \\ \therefore x = \frac{32 \times 500}{261} = 61.3 \text{ grams oxygen.} \end{array}$$

As an example of the converse operation,—Let it be required to calculate what quantity of manganese must be used to obtain one kilogram of oxygen.

Since 32 grams of oxygen require 261 grams of manganese

1 gram „ „ requires  $\frac{261}{32}$  „ „

$\therefore$  1 kilogram (= 1000 grams),  $\frac{261}{32} \times 1000$ .

*Ans.*—Quantity of manganese =  $\frac{261}{32} \times 1000 = 8156\frac{1}{4}$  grams.

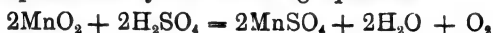
Or, it may be found from the equation  $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$  by simple proportion, thus—

$$\begin{array}{ccccccc} \text{Weight of O}_2 & : & \text{given weight} & : & \text{weight of} & : & \text{required wt.} \\ & & \text{of oxygen.} & & 3\text{MnO}_2 & & \text{of manganese.} \\ \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} & & \underbrace{\hspace{1.5cm}} \\ 32 & & 1000 & & 261 & & x \\ \therefore x = \frac{261 \times 1000}{32} = 8156\frac{1}{4} \text{ grams.} \end{array}$$

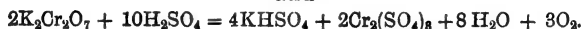
$\therefore$  Quantity of manganese peroxide = 8.15625 kilograms.

Other peroxides, such as plumbic peroxide,  $\text{PbO}_2$ , and baric peroxide,  $\text{BaO}_2$ , also lose part of their oxygen when strongly heated, and are reduced to a lower condition of oxidation, as for example  $\text{BaO}_2 = \text{BaO} + \text{O}$ .

Oxygen can also be prepared by the action of sulphuric acid on manganic peroxide as well as by the action of the same acid on potassium anhydro-chromate when heated to a definite temperature, the reactions which take place being represented by the following equations:—



and



In fact, sulphuric acid itself may be employed as a source of oxygen gas, for when the concentrated acid is allowed to trickle over bricks heated to bright redness, the acid is decomposed into oxygen, sulphurous anhydride and water vapour. The acid, in fact, undergoes *dissociation*:—



Oxygen is also produced by the electrolysis of water, and as a product of the action of vegetable life on the atmosphere.

### SULPHUR. S = 32.

Sulphur, Selenium, and Tellurium form a group of elements resembling oxygen in their chemical relations. In their combinations with hydrogen, they play the part of *dyad* elements, although their active atomicities are more frequently *tetrad* and even *hexad*—as in the common oxides of sulphur,  $\text{SO}_2$  and  $\text{SO}_3$ , respectively.

This group (termed the sulphur group) exhibit gradational differences in their atomic weights and specific gravities, &c., exactly similar to those which characterise

the three members, chlorine, bromine and iodine, of the halogen group of elements.

Sulphur	S	= 32	} 79.8 = mean.
Selenium	Se	= 79	
Tellurium	Te	= 128	

**Occurrence.\***—Sulphur is found abundantly in the free state in the volcanic districts, more especially in Sicily and Iceland. The Sicilian sulphur, which is usually mixed with various rocky materials (such as gypsum, limestone, marl, and celestine), is largely imported into England under the name of native sulphur, or *brimstone*.

Native sulphur is freed from its earthly impurities by repeated dry distillations or sublimations, the condensed vapour being called flowers of sulphur; it is either stored in that state, or melted and cast in cylindrical moulds into sticks, called roll sulphur. Besides occurring in the native state, sulphur is frequently met with in combination with metals, forming an important class of *mine* products termed sulphides, or sulphurets, those of iron ( $\text{FeS}_2$ ), copper ( $\text{CuS}_2$ ), lead ( $\text{PbS}$ ), and Zinc ( $\text{ZnS}$ ) being the most common. It is also found as a constituent of the sulphates (or oxidized sulphides), the sulphates of calcium (gypsum), barium (heavy spar), magnesium (Epsom salt) being of most frequent occurrence. Sulphur in minute quantities is present in vegetable and animal tissues.

**Properties.**—Sulphur is a brittle solid of a lemon yellow colour, and it is a non-conductor of heat and electricity. It emits a peculiar odour when rubbed with the hand, at the same time becoming negatively electrified. It is

\* Selenium and Tellurium are *rare* elements; they are only obtainable in small quantities, and, with the exception of the recent application of selenium in the construction of the *photophone*, have not been largely applied to useful purposes. The chemistry of these two elements will therefore be omitted from the present course.

tasteless and insoluble in water, it dissolves very slightly in alcohol and ether, but readily in the bisulphide of carbon.

Like oxygen, this element affords an example of *allotropism*, but instead of two different states of molecular arrangement, sulphur presents three well-known varieties. There are two crystalline modifications and one amorphous variety:—

*Crystalline Modifications.*—

Octahedral Sulphur—Specific gravity 2.05

Prismatic Sulphur—Do. 1.98

Native sulphur occurs in minute octahedral crystals, as well as in an apparently amorphous condition. The second crystalline modification (prismatic sulphur) is obtained when ordinary roll sulphur is melted, and (while cooling slowly the crust which forms on the surface being broken open) the liquid sulphur poured out on a slab. But the prismatic crystals thus obtained, on exposure to the air, are slowly changed into the octahedral variety of sulphur, heat being at the same time evolved.

*Amorphous Modification.*—

A third modification of sulphur, or *amorphous sulphur*, is obtained when melted sulphur at about 230° C. is suddenly cooled by pouring into cold water. When treated thus, sulphur changes into a soft plastic mass of an amber brown colour, resembling caoutchouc, and its specific gravity is reduced to 1.95. In this state it is insoluble in carbon-disulphide. After the lapse of a short time, however, the plastic condition is lost, and the sulphur recovers its yellow colour and characteristic brittleness, and at the same time the specific gravity rises, so that it may be said to return to the prismatic condition. This change of condition can be brought about

suddenly by heating the plastic material to  $100^{\circ}\text{C}$ ., when the change is accompanied with evolution of heat.

When united with positive radicles, sulphur is usually a *dyad* element and the *analogue* of oxygen, as for example :—

Oxides .....  $\text{H}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{KHO}$ ,  $\text{CO}_2$ , &c.

Sulphides.....  $\text{H}_2\text{S}$ ,  $\text{K}_2\text{S}$ ,  $\text{KHS}$ ,  $\text{CS}_2$ , &c.

Sulphur inflames at a low temperature,\* burning with a pale blue flame when heated in contact with air or oxygen, or any substance such as nitre, which readily gives off oxygen—the product being the ordinary dioxide of sulphur,  $\text{SO}_2$ ; it is this gas which yields the suffocating odour when a lucifer match is ignited.

Sulphur is employed in the arts in the manufacture of oil of vitriol, matches, and gunpowder, &c. The fumes of burning sulphur act as an effective bleaching agent as well as deodorizer and antichlore.

The following are the more important compounds of sulphur with hydrogen and oxygen :—

Sulphuretted Hydrogen .....  $\text{H}_2\text{S}$ .

Sulphurous Anhydride.....  $\text{SO}_2$ .

Sulphurous Acid .....  $\text{H}_2\text{SO}_3 (= \text{H}_2\text{O} + \text{SO}_2)$ .

Hyposulphurous Acid .....  $\text{H}_2\text{SO}_2$ .

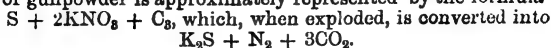
Sulphuric Anhydride .....  $\text{SO}_3$ .

Sulphuric Acid.....  $\text{H}_2\text{SO}_4 (= \text{H}_2\text{O} + \text{SO}_3)$ .

Thio-Sulphuric Acid .....  $\text{H}_2\text{SO}_3\text{S}$ .

The sodium salt of the last acid is popularly, though wrongly, termed “hyposulphite of soda.”

\* Hence its use in the manufacture of gunpowder; the composition of gunpowder is approximately represented by the formula



The sudden production of large volumes of nitrogen and carbon dioxide at a high temperature explains the secret of the propulsive force of gunpowder.



Both  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are known to occur among the gases ejected by volcanoes, and by their mutual reaction sulphur is deposited, thus :—



This explains the special occurrence of sulphur in volcanic districts.

Sulphur forms two compounds with Hydrogen, Hydrogen Sulphide ( $\text{H}_2\text{S}$ ) and Hydrogen Persulphide ( $\text{H}_2\text{S}_2^*$ ). The former only is of sufficient importance for notice in a first course of chemistry.

Hydrogen sulphide (sulphuretted hydrogen) is usually prepared by the action of dilute sulphuric acid on sulphide of iron (ferrous sulphide)  $\text{FeS}$ .



The gas can be collected over warm water, being rather soluble in cold water, forming an acid solution; or, if a solution of the gas be required, it should be passed through a series of Woulfe's bottles containing distilled water.

This gas, notwithstanding its bad smell, is of great use in Analytical Chemistry. As an illustration of its peculiar use in this way I will now pass a current of sulphuretted hydrogen through the series of five similar bottles, arranged in order before you.

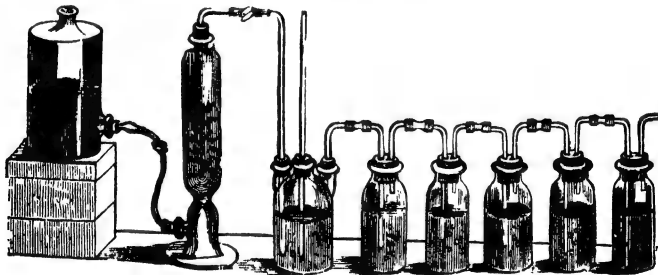


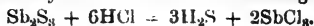
Fig. 20.

The first bottle contains a solution of copper-sulphate, the second a solution of arsenic, the third a solution of antimony, the fourth a salt of lead, and the fifth an alkaline solution of zinc.

\*  $\text{H}_2\text{S}_2$  is chiefly interesting as being the analogue of Hydrogen peroxide  $\text{H}_2\text{O}_2$ . It is an unstable oily liquid.

The copper compound turns *brownish-black*, the arsenic *yellow*, the antimony *orange*, the lead *black*, and the zinc *white*, because coloured sulphides of the respective metals are formed.  $\text{H}_2\text{S}$  is thus a valuable reagent for precipitating metals from solutions of their salts.

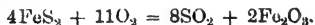
This gas is obtained in a purer condition by acting on antimony sulphide with dilute hydrochloric acid and heating the mixture.



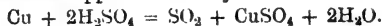
Prepared from  $\text{FeS}$  and oil of vitriol it is usually accompanied by a small quantity of free hydrogen, and sometimes arseniuretted hydrogen. The iron sulphide, being usually artificially prepared by melting together iron and sulphur, frequently contains some *uncombined* iron, which with the acid would give hydrogen gas. Oil of vitriol also frequently contains arsenic. When nascent hydrogen and sulphur vapour are brought together, this compound is formed. It is also formed by the action of zinc on concentrated sulphuric acid, hence an additional reason for diluting this acid in the ordinary method of preparing hydrogen. Sulphuretted hydrogen is a highly poisonous gas, and is given off from the sewers of large cities in considerable quantities. Its presence in the atmosphere of foul drains and water closets can easily be detected by its blackening white blotting paper which has been previously soaked in a solution of acetate of lead—the so-called sugar of lead of the druggists.

We must now content ourselves with manufacturing small quantities of sulphurous and sulphuric oxides and acids, leaving the study of the remaining sulphur compounds for a future occasion.

*Sulphurous Anhydride* ( $\text{SO}_2$ ) is obtained for preparing sulphuric acid by burning sulphur in air ( $\text{S} + \text{O}_2 = \text{SO}_2$ ); or by roasting iron pyrites in a current of air:—



For Laboratory purposes it is most easily prepared by heating sulphuric acid with copper or mercury:—



The gas may be washed by passing it through a small quantity of water previous to collecting it in water, with which it forms a solution of *sulphurous acid*, having, like carbonic acid, the *hypothetical* composition  $\text{H}_2\text{SO}_3$  ( $\text{H}_2\text{O} + \text{SO}_2$ ). The dry gas is a non-supporter of combustion, and is irrespirable; it is, in fact, sometimes employed as a fire extinguisher. Like chlorine it is employed as a *bleaching agent* for straw and woollen goods, the fibre of which would be attacked by chlorine. Owing to its great power of combining with

oxygen, it is useful as a preventive of fermentation and as a disinfectant for sick rooms.

*Sulphuric acid* (hydrogen sulphate) is the most important compound of sulphur with oxygen and hydrogen. It is the most powerful of all the hydrogen salts, or acids. Sulphuric acid is manufactured on a large scale in leaden chambers. Sulphur dioxide ( $\text{SO}_2$ ) is supplied to the chamber in company with steam and oxides of nitrogen, which, in the presence of water vapour and air act as carriers of oxygen from the air to complete the oxidation of the sulphuric anhydride. On a small scale the processes going on in the leaden chamber may be imitated as follows :—



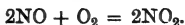
Fig. 21.

The large globular flask representing the leaden chamber has led into it, by glass tubes from the three smaller flasks, water vapour (steam), sulphur dioxide and nitroso-nitric anhydride  $\text{NO}_2$  (or perhaps a mixture of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ ).

By the joint action of oxygen and steam the sulphurous gas is converted into sulphuric acid  $\text{H}_2\text{SO}_4$ .



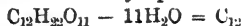
The nitric oxide ( $\text{NO}$ ) formed takes up fresh oxygen from the air and  $\text{NO}_2$  is reformed.



This again meeting with additional sulphurous gas gives up oxygen to it, converting it as before into sulphuric acid, which dissolves in the excess of water at the bottom of the vessel, and so on keeping up these reactions continuously till the process is completed.

When sulphur dioxide and oxygen are passed together through a red-hot platinum tube (packed with asbestos), the two gases combine with the production of *sulphuric anhydride*,  $\text{SO}_2 + \text{O} = \text{SO}_3$ , which is a white needle-like crystalline solid, which if thrown into water hisses like a hot iron quenching, and combines with the water to form hydrogen sulphate,  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ .

Sulphuric acid has a great desire for water, hence it has a very destructive action on organic matter usually causing it to *char* or carbonise. This property may be illustrated by pouring a sufficiency of strong sulphuric acid over a syrup of cane sugar,



when a large mass of carbon will be set free. It is the strongest acid known, and expels all other acids from their combinations. It unites with bases to form *Sulphates*, some of which are formulated below—the *insolubility* of barium, strontium and lead sulphates serving as *tests* for distinguishing this acid from others.

### *Familiar Sulphates.*

Sodic sulphate	Glauber's salt	$\text{Na}_2\text{SO}_4$
Magnosic sulphate	Epsom salt	$\text{MgSO}_4$
Calcic sulphate	Alabaster, gypsum, selenite, plaster-of-Paris	$\text{CaSO}_4$
Baric sulphate	Heavy spar, permanent white	$\text{BaSO}_4$
Zincic sulphate	White vitriol	$\text{ZnSO}_4$
Cupric sulphate	Blue vitriol (bluestone)	$\text{CuSO}_4$
Plumbic sulphate	Lead vitriol	$\text{PbSO}_4$
Ferrous sulphate	Green vitriol, or copperas	$\text{FeSO}_4$
Dipotassic aluminic tetrasulphate	Common alum	$\text{K}_2\text{Al}_2(\text{SO}_4)_4$
Sodic thiosulphate	Hyposulphite of soda (antichlor)	$\text{Na}_2\text{S}_2\text{O}_3$

## CHAPTER XIII.

### HYDROGEN and OXYGEN.

We shall now revert to some simple experiments with *combined* hydrogen and oxygen, and show that water is the result.

That the inflammability of hydrogen in air is due to its powerful affinity for oxygen may be demonstrated by the following experiments :—

I take a very strong gas jar, about the capacity of one pint (a soda-water bottle answers the purpose excellently), and into this jar I shall presently decant, under the water in the pneumatic trough, 2 measures of hydrogen and 1 measure of oxygen. I shall then cover the mouth of the jar with a ground-glass plate, and place it on the table with its mouth upwards. This being done, I take the jar in one hand, and, removing the glass-plate, apply a lighted taper to its mouth with the other. You observe the result : the two gases instantly combine with an explosion\* accompanied by a loud noise similar to the report of a pistol ; in fact it is such a mixture that is fired by an electric spark in the apparatus we call the 'Electric Pistol.' The compound produced by the combination of the hydrogen and oxygen in this experiment is water : this may be proved by exploding the

\*No dangerous consequences result from this explosion if a sufficiently strong jar be used ; it is advisable to wrap the jar in a towel before applying the lighted taper. A jar of *sheet tin* may be employed with perfect safety.

mixture by an electric spark in a strong reservoir of glass, such as that used by Cavendish in 1781, when the composition of water was first accurately determined. The reservoir is first exhausted of air by means of an air-pump, and then filled with the mixed gases in the proportion of 2 volumes of hydrogen to 1 volume of oxygen from a transferring jar (see Fig. 22). This being done, the stop-cock is shut, and the mixture is exploded by connecting one of the platinum wires which are fixed in the stopper with the exterior of a charged Leyden jar, and the other with the knob: on examining the reservoir after the mixture has been fired, the gases are found to have completely disappeared, producing by their combination a volume of steam which, if measured at the same temperature and pressure, would be found *exactly equal* to the two volumes of hydrogen used; the steam thus produced is quickly condensed into water by the cold and pressure it experiences in the reservoir, from which it can be taken and its properties examined. If any other proportions of these gases than those already mentioned be transferred to this apparatus, which goes by the name of 'Cavendish's Eudiometer,' on examining its contents after firing the mixture there will always be found remaining the exact quantity of the particular gas which has been added in excess of the aforementioned proportions.

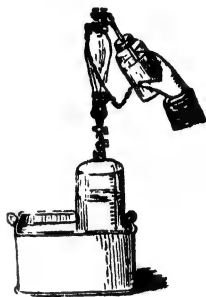


Fig. 22.

In the ordinary bottle for generating hydrogen, if the bent delivery tube be replaced by a long glass tube drawn out to a fine point (or, better still, a common brass blow-pipe, which should be straightened), the hydrogen may

be ignited\* at the point of the tube from which it escapes into the air (see Fig. 23). If now while the hydrogen is burning, I bring a tolerably large bell-shaped glass jar, perfectly dry and bright, over the flame, the surface of the glass (as you perceive) becomes dimmed, due to the condensation of small drops of water by the cold glass. By keeping the glass jar cool for a short time, I can thus collect a sufficient number of drops to satisfy you that it is water that is produced by the combustion of hydrogen in air. Now, as by Cavendish's experiment it was shown that water is composed of hydrogen and oxygen, it is therefore evident that the combustion of hydrogen in air is due to its combination with oxygen to form water.

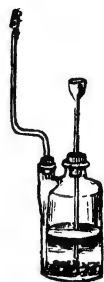


Fig. 23.

With the apparatus just described, which is called Priestley's 'Philosophical Candle,' a very amusing experiment may be made by covering the hydrogen flame with a thin glass, porcelain or metallic tube open at both ends; when the tube is held in a vertical position and depressed sufficiently over the jet, the flame elongates, in consequence of the draught caused by the tube acting the part of a chimney, and a musical sound is produced, which varies with the size of the jet, and with the dimensions of the tube. This arrangement is sometimes called the 'Chemical Harmonicon.' The sounds are produced by a series of small explosions, which take place in rapid succession in the tube, and which are caused by the hydrogen combining with oxygen from the air. These explosions set the air in a state of vibration, which it propagates to the ear, thereby producing the sensation of sound.

\* The air should be allowed to escape out of the bottle before igniting the hydrogen, if not, the mixed gases in the bottle may explode with violence sufficient to break it.

In all the previous experiments illustrating the great affinity of hydrogen for oxygen, whether pure or mixed with the nitrogen of the air, heat was applied by means of a lighted taper or of an electric spark before combination commenced; but once begun, sufficient heat was evolved to continue the act of combination. In the year 1824 it was discovered by Dobereiner that hydrogen and oxygen might be made to combine without the actual application of heat, by bringing the mixed gases in contact with spongy platinum, *i.e.* metallic platinum in a very fine state of division. Utilising this discovery, Dobereiner constructed a lamp (Fig. 24) for giving an instantaneous light, in which hydrogen forms the combustible material. The hydrogen is developed in the usual way, by the action of zinc on hydrogen sulphate, and is allowed to accumulate in an inverted glass jar, attached to the cover of the outer vessel by means of a brass jet and stop-cock. By depressing a lever in connection with the stop-cock the hydrogen escapes, and impinges on a little pellet of spongy platinum, which is placed in a brass cap immediately in front of the jet. The hydrogen meeting with oxygen in contact with the spongy platinum gradually combines with it,\* and finally bursts into flame, in which a candle or taper may be lighted. This apparatus has fallen into disuse since the invention of lucifer matches.

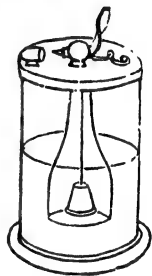


Fig. 24.

In consequence of the great affinity hydrogen has for

\* It has been shown by Liebig that a cubic inch of spongy platinum can condense in its pores 800 cubic inches of oxygen. Hence, as heat is evolved by the condensation of the volume of a gas, the temperature necessary to initiate the combination of the oxygen and hydrogen may be evolved in this way.



oxygen, it forms a powerful *reducing agent*, and is employed by the analytical chemist for reducing metallic oxides to the metallic state. The following experiment will illustrate this useful application of hydrogen gas.

I have selected for this purpose the oxide of copper known as the black oxide, it being very unlike the metal it contains in combination with its oxygen. The oxide is placed in the bulb of a hard German glass tube, called a reduction tube, which is made red-hot by applying a spirit-lamp to it. By conducting a stream of hydrogen from the generating bottle, first through a drying tube containing chloride of calcium, and then over the copper oxide in the reduction tube (see Fig. 25), the hydrogen takes up (combines with) the oxygen it meets with in the

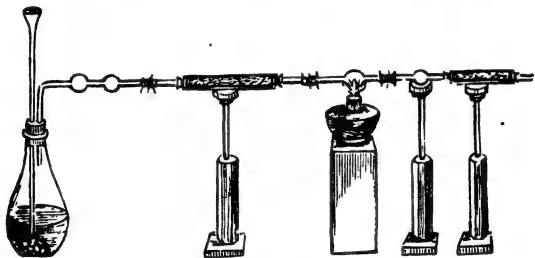


Fig. 25.

red-hot black oxide of copper. It is necessary that the oxide of copper be maintained at a red heat, since a certain temperature is required to determine the combination of hydrogen and oxygen; and, besides, heat tends to overcome the affinity of the oxygen for the copper, inasmuch as it reduces the cohesion between the particles of the cupric oxide.

You observe that the substance in the bulb of the reduction tube has changed its original black for its present red colour. I shall now remove some of this red stuff from

the tube, and let you examine it and satisfy yourselves that it is really copper. Under the hammer it burnishes like plate copper.

By collecting the gas that escapes from the open end of the reduction tube, it may further be proved that the hydrogen has really taken up the oxygen in its passage over the oxide of copper, and with it formed water. The following equation represents the decomposition of a molecule of cupric oxide, with the replacement of its copper by hydrogen :—



The two dashes written over the symbol of the copper are intended to denote that 1 atom of copper is *equivalent in combining power* to 2 atoms of hydrogen.

You must have noticed that the flame of burning hydrogen yields but very little light;\* this, however, is compensated for by the great amount of heat it evolves.

A kilogram of hydrogen, in combining with the necessary quantity of oxygen (8 kilograms) to form water, evolves 34,462 thermal units, or degrees of heat,—*i.e.* the quantity of heat developed by the complete combustion of 1 kilogram of hydrogen in oxygen, is capable of raising the temperature of 34,462 kilograms of water from 0° C. to 1° C. By converting these *units of heat* into *units of work* we will gain some idea of the enormous amount of *force* produced by *chemical action*. The mechanical equivalent of a unit of heat being 424 kilogram-meters, each unit of heat developed by the combustion of hydrogen in oxygen is capable of doing 421 units of work, and therefore 34,462 units of heat are capable of performing  $424 \times 34,462 = 14,611,888$  units of work,—*i.e.* upwards of  $14\frac{1}{2}$  millions of kilograms raised through a height of one meter.

\* Perfectly pure hydrogen burns with a pale reddish-brown flame.

If the combustion of a kilogram of hydrogen in oxygen be assumed to occupy a *second of time*, the work produced by the combination of one kilogram of hydrogen with 8 kilograms of oxygen would be equivalent to

$$\frac{14,611,888}{75} = 194,825 \text{ Horse Power,}$$

or, in other words, the force stored up in a kilogram of hydrogen gas is, very nearly, equivalent to the combined strength of two hundred thousand horses.

This calculation gives a fair idea of the strength of the chemical force, since the strength of the chemical attraction between any two substances is proportional to the quantity of heat evolved by their combination, or (which is found to be the same) to that needed to separate them from combination.

If hydrogen and oxygen be mixed together in the proportion of two volumes of hydrogen to one volume of oxygen, and the mixture ignited while escaping from a capillary tube, they yield the most intense heat at present obtainable by chemical action; it is only exceeded by the heat of the electric lamp and by that of the sun's rays when concentrated by a powerful lens. The heat produced is sufficient to fuse platinum and silica, and even to convert some very refractory solid substances into the gaseous state. Such a mixture is used in the apparatus called the *oxy-hydrogen blowpipe*. The oxy-hydrogen flame may be produced without the use of this expensive but safer apparatus, as follows :—

I light the 'Philosophical Candle,' and, having filled a bladder which has been fitted with a brass jet and stop-cock with oxygen, I place it on a block of wood in such a position that the jet attached to the bladder may be on a

level with the nozzle of the hydrogen jet (see Fig. 26).

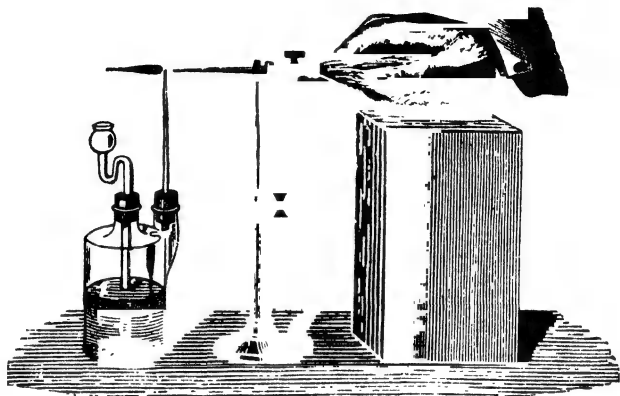


Fig. 26.

Now by gently pressing the bladder with my hand the oxygen is forced out of the brass jet, and it blows the hydrogen flame in a horizontal direction.

The flame, you observe, gives scarcely any light, but that it evolves intense heat is manifested by its melting this piece of platinum wire,—since platinum requires higher temperature to melt it than any other metal does.

That the presence of an *incandescent solid* in flame increases its power of evolving light, is well exemplified by holding a piece of lime in this flame; the lime, becoming incandescent, emits a most dazzling bright light. A light of this kind was first employed during the Trigonometrical Survey of Ireland, by Captain Drummond, for making observations with the Theodolite at long distances; it is now much used for illuminating microscopic objects and magic-lantern slides, &c., under the name of the *oxy-hydrogen lime-light*, with an exhibition of which I shall conclude this lecture.

## CHAPTER XIV.

### WATER.

Molecule,  $\text{H}_2\text{O} = 18$  ; Density = 9.

**Occurrence.**—The modes of occurrence of water are so well known to every one as scarcely to need description. It occurs in a tolerably pure state in the rain and snow that fall in the open country far away from large towns. *Ice* is, almost invariably, pure water in the *solid form*. Most of the waters we meet with on the surface of the globe contain various foreign substances in solution. These substances, though not chemically combined with the components of the water in which they are dissolved, impart to it various qualities, such as softness, hardness, medicinal properties, &c. The chemistry of such waters, however, may be advantageously postponed till we have learned something about *those substances* to the presence of which (in solution) are due the qualities in question.

**Purification.**—For chemical purposes pure water must be employed : it is usually prepared by distilling ordinary (im-pure) water. The process of distillation is exhibited on a small scale by boiling water in a retort, the neck of which passes into a receiver (see Fig. 27). The receiver is kept cool by being placed in a vessel of cold

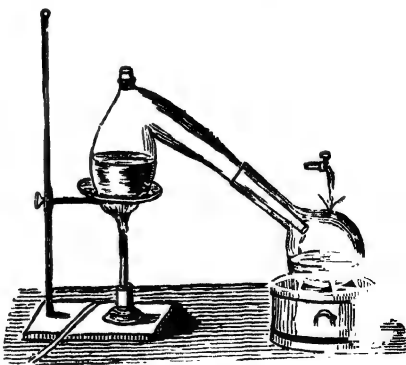


Fig. 27.

water, while continued drops of cold water are allowed to fall on it from a cistern standing above. The steam passes into the receiver, where it is condensed into water, by the loss of its latent heat. The cold water in the basin absorbs the heat from the steam, and thereby becomes warm itself, for which reason it is necessary to have the condensing water renewed by a stream of drops from a cistern of cold water.

When pure water is required in larger quantities, a copper still and condenser (Fig. 28) are used. Rain water collected in the country may sometimes be had pure enough for chemical experiments.

**Composition—Formation:**—That water is composed of hydrogen and oxygen has already been demonstrated in considering one of the properties of hydrogen, viz. its great affinity for oxygen. An experiment in confirmation of this statement, however, will not be without instruction. If a tolerably large metallic ball be held thus (Fig. 29) over a jet of burning hydrogen for a few seconds, water will be formed by the condensation of the water-gas pro-

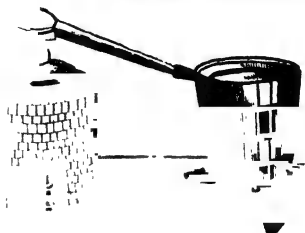


Fig. 28.



Fig. 29.

duced by the combination of the hydrogen with the oxygen of the air. A drop of water, as you may now observe, hangs from the lowest point of the surface of the ball. The steam parts with its latent heat to the cold metallic ball, and is thus reduced to the liquid state.

We have already noticed that when dry hydrogen was passed over a black substance, which was known to contain two elements only, namely, copper and oxygen ( $\text{CuO}$ ) the copper alone was left, the oxygen having combined with the hydrogen to form water.

Cavendish has taught us that water is produced by exploding (by means of an electric spark) a mixture of oxygen and hydrogen in his Eudiometer. His experiment has also taught us that when these gases were mixed in the proportion of two volumes of hydrogen to one volume of oxygen, nothing but water remained in the reservoir after they were exploded. We are thus led to conclude that water is composed of two volumes of hydrogen and one volume of oxygen. It was in this manner, that is, by the method of *synthesis*, that the composition of water was first determined (so late as A.D. 1781) by Cavendish, who weighed the glass reservoir before and after the explosions, and thus found that the weight of the water produced was exactly the same as that of the mixed gases which combined to produce it.

Since the time of Cavendish the composition of water has been determined, both *analytically* and *synthetically*, by numerous and exact experiments, which result in a confirmation of the original conclusion of Cavendish, namely, that water is composed of hydrogen and oxygen in the proportion of two volumes of the former to one of the latter. It will be interesting and instructive to verify this statement by the following experiment:—

We may *analyse* water by means of the electric current. For this purpose I half fill this glass vessel (Fig. 30) with water, which has been acidulated with about one-tenth of its volume of hydrogen sulphate (sulphuric acid). The acid enables the water to conduct the electric current better than it otherwise would. The graduated tubes, being also filled with the acidulated water, are inverted over the two small platinum plates, which you see in this glass vessel. These platinum *plates* are connected with platinum *wires* which pass through the bottom of the vessel. I now bring the platinum wires into contact with the terminal wires of a galvanic battery (three or four cells of Grove's are sufficient), and notice that an evolution of gas takes place from the surface of each of the platinum plates. I shall presently prove (by immersing a lighted taper in each tube) that it is oxygen that is collecting in the tube which stands over the plate in connection with the platinum or *positive end* of the battery, and hydrogen that is collecting in the tube which stands over the plate in connection with the zinc or *negative end* of the battery. One of the tubes being now nearly filled with gas, I stop the decomposition of the water by breaking the contact of the platinum plates with the terminal wires of the battery. You observe now that the volume occupied by the gas in one tube is about double that occupied by the gas in the other. It should be exactly double were oxygen and hydrogen *equally soluble* in water. Oxygen is about 1 per cent. more soluble in water than hydrogen, hence the bulk of hydrogen obtained in this experiment proves to be a fraction more than double that of the oxygen.



Fig. 30.

Let us now examine the properties of the gases con-



tained in these two tubes. The taper, you observe, is extinguished by the gas which occupies the larger bulk; the gas itself, however, burns at its surface of contact with the air, consequently (having already satisfied ourselves by many previous experiments that water contains nothing else besides oxygen and hydrogen) this is the hydrogen. Into the other gas I plunge a glowing-red chip of wood. You notice that it bursts into flame. The taper is not extinguished by it, but burns with greater brilliancy. Mixed with hydrogen it burns with an explosion when a light is presented to it. Hence we may say that this gas (*i.e.* the one having the smaller volume) is the oxygen. This experiment, therefore, teaches us—due allowance being made for the greater solubility of oxygen—that water is composed of two volumes of hydrogen united with one volume of oxygen.

This conclusion may be confirmed by a *synthetical* experiment. The apparatus to be used (a modification of that used by Cavendish) is called a Eudiometer, and consists of a graduated glass tube, into one end of which are melted two platinum wires (see Fig. 31). The tube must first be filled with mercury, and then inverted in a long narrow jar, or mercurial trough, filled with the same metal. Hydrogen may now be admitted into the tube. I shall admit 50 measures of it. Now I shall admit any quantity of oxygen you please: let us say 50 measures also. Here, then, I have got in this tube 50 volumes of hydrogen and 50 volumes of oxygen, or in other words, these gases are mixed together in equal proportions. I must now ask you carefully to notice the volume of the gas remaining after I have passed an electric spark through the mixture. Connecting one of the platinum wires with the outer

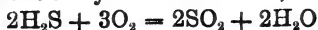


Fig. 31.

coating of a charged Leyden jar, and approaching the knob to the other wire, the spark now passes, and the mixture, you observe, is suddenly exploded with the production of flame, which is evidence that combination has taken place. The bottom of the eudiometer tube, which rests on a caoutchouc pad, may now be opened, so as to admit the mercury. This being done, the mercury rises rapidly into the tube, and, as you may now perceive, comes to a standstill about the graduated mark 25. Hence we have left of the 100 volumes of the mixture only 25 volumes of gas. That this residual gas is oxygen is easily shown by its power of supporting (without exploding) the combustion of a glowing chip of wood, &c. The water produced is deposited like dew on the sides of the tube, and occupies about  $\frac{1}{2,000}$ th part of the volume occupied by its components; we may, therefore, neglect it in measuring the volume of the residual gas. We thus see that 50 volumes of hydrogen require exactly 25 volumes (or half its own bulk) of oxygen in order to burn it *completely*; we may, therefore, conclude that any quantity of water is composed of a certain quantity of hydrogen united to half its own bulk of oxygen. Water is *formed* whenever any compound containing hydrogen is burned in oxygen or air; and it most frequently happens that the other elements which are in combination with the hydrogen become oxidised at the same time. The combustion of Marsh gas ( $\text{CH}_4$ ), for example, in oxygen may be represented thus—

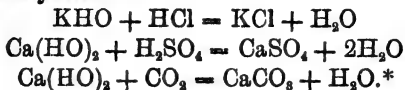


Sulphuretted hydrogen likewise when burned in oxygen yields sulphurous anhydride and water, thus—



Water occurs as a secondary product in numerous

chemical reactions, as in the case of the action of acids on metallic hydrates—



Water is likewise formed when certain metallic oxides are heated in a current of hydrogen gas. Thus cupric oxide, when heated with hydrogen, yields water and metallic copper,



a reaction which provides a simple method for determining the *gravimetric*, as distinguished from the *volumetric*, composition of water.

From the composition of water *by volume* we can deduce its composition *by weight*; for since oxygen is sixteen times as heavy as hydrogen, bulk for bulk, and since they combine to form water in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, therefore the proportions by weight in which they combine are as 2 to 16. Hence, since the atomic weight of hydrogen = 1, and that of oxygen = 16, each molecule of water may be represented as composed of 2 atoms of hydrogen and 1 atom of oxygen, which fact is more concisely expressed by the formula  $\text{H}_2\text{O}$ .

That the proportion by weight of the hydrogen to the oxygen in water is correctly represented by 2 : 16, may further be proved by repeating the experiment of reducing cupric oxide with hydrogen. If we take a known weight of copper oxide and heat it to redness in the presence of an atmosphere of dry hydrogen gas, after a little time all the oxygen will have combined with hydrogen to form water : by collecting and weighing all

\* This reaction explains the 'setting' and 'hardening' of mortar, as well as the *dampness* of recently-plastered rooms.

the water formed, and deducting the weight of the oxygen (*i.e.* the loss in weight of the copper oxide) from that of the water, the remainder will be the weight of the hydrogen which has entered into combination with the oxygen, the weight of which is known from the loss in weight of the oxide of copper. In this experiment the water which is formed is usually collected by being conducted into a tube packed with fragments of chloride of calcium (as in Fig. 25), by which it is absorbed; and the increase in the weight of this tube is evidently the weight of the water produced by the combination of the oxygen of the copper oxide with hydrogen; the excess of hydrogen is allowed to escape into the air.

If  $a$  be the weight of the reduction tube and the oxide of copper it contains; and  $a'$  be the weight of the tube and copper when the oxide is completely reduced; if, too,  $c$  and  $c'$  be the combined weights of the chloride of calcium tube and its contents at the commencement and termination of the experiment, respectively, the quantity of water formed will evidently be  $c' - c$ ; from this subtracting the oxygen (which is represented by  $a - a'$ ) we get the hydrogen to be  $(c' - c) - (a - a')$ .

When the necessary weighings, &c., are performed with accuracy, the ratio of  $(c' - c) - (a - a')$  to  $a - a'$  is found to be as 1 to 8, which is the same as 2 : 16.

Dumas, who made a number of very accurate experiments in the manner I have just described, has found that in 100 parts by weight of water there are—

of Hydrogen.....	11.1111}	parts by weight.
of Oxygen.....	88.8889}	

These numbers are plainly in the proportion of 1 : 8, or 2 : 16, which are those already deduced from the known volumetric composition of water-gas.

**Properties.**—Water, though most commonly met with in the form of a liquid, is capable of assuming both the solid and gaseous conditions.

Hydrogen is one of the most inflammable substances in Nature, yet *water cannot be set on fire*; oxygen, on the other hand, causes bodies to burn with great brilliancy, whilst *water extinguishes combustion*. Water thus affords a most striking illustration of the fact that compound bodies possess properties different from those of their components.

When tolerably pure, water presents a bluish-green colour to the eye, especially when seen in large quantities, such as the waters of the ‘deep blue sea.’ In muddy waters this colour is not visible. The lakes of Switzerland are remarkable for the blue colour of their waters.\* Ice, too, exhibits the same colour when seen in large masses, such as glaciers, icebergs, &c. Pure water is tasteless and odourless.

Water is slightly compressible. Oersted has found its compressibility to be proportional to the compressing force, and for an increase of pressure equal to one atmosphere to be *fifty-three-millionths* ( $\frac{53}{1,000,000}$ ) of its bulk. It is also elastic, for when the pressure is removed it returns to its original bulk.

All gases are soluble in water to a greater or less extent: increase in the temperature of the water is generally accompanied by a decrease in the amount of gas dissolved; for example, 100 volumes of water at 0° C. will dissolve 4 volumes of oxygen, while the same water at 15°·5 C. (60° F.) is capable of dissolving only 3 volumes of oxygen.

\* Professor Tyndall appears to have shown that the blue colour of water, as well as that of the atmosphere, is due to the effect on light of the minute particles of dust held in mechanical suspension.

When gases are mixed together mechanically, the quantity of each gas which will dissolve in water is dependent on its proportion in the mixture and its rate of solubility (co-efficient of absorption): thus when air is dissolved in water about one-third of the dissolved air is found to be oxygen, and two-thirds nitrogen.\*

Water absorbs the same volume of gas in the condensed state as of gas under the ordinary atmospheric pressure; the condensed gas, however, escapes when the excess of pressure is removed—a bottle of soda or aerated water presents a familiar illustration.

The elements of water enter into combination with numerous substances, and bodies of which they form essential ingredients are frequently termed *hydrates*. Calcium oxide (quicklime) when brought into contact with water combines with it with great violence, exhibiting phenomena somewhat like those of combustion (such as evolution of heat, &c.). The compound thus formed, commonly known as slaked lime, is calcium hydrate,  $\text{CaOH}_2\text{O}$ , or  $\text{CaH}_2\text{O}_2$ , or  $\text{Ca}(\text{HO})_2$ .

Water combines directly (as water) with many salts, from which it can be driven off by heat. Water thus combined appears to impart to some salts the property of forming crystals of a distinct geometric form. It is hence termed *water of crystallization*. Thus a molecule of calcium sulphate (sulphate of lime) combines with two molecules of water,  $\text{CaSO}_4 + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . It is for this reason that Plaster of Paris, *sets* when wet with water.

Some salts combine with several proportions of water and retain its successive molecules with different degrees of force. Thus crystallized magnesium sulphate (or Epsom

\* This fact is used as an argument to prove that the atmosphere is a mechanical mixture, and not a chemical compound.

salts),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , may be converted by exposure over strong hydrogen sulphate into  $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ ; by heating to  $130^\circ \text{C}$ . it is converted into  $\text{MgSO}_4 \cdot \text{H}_2\text{O}^*$ ; and the whole of the water is driven off by exposure of the original crystals to a temperature of  $210^\circ \text{C}$ .

The effects of heat on water, being in some respects peculiar, are particularly worthy of attention.

If we take a certain weight of water (a kilogram for instance), and measure its volume at  $0^\circ \text{C}$ ., and if while gradually heating the water its volume be measured from time to time, it will be found that the volume of the water becomes less and less till its temperature arrives at  $4^\circ \text{C}$ .; or in other words, water contracts in bulk, while its temperature is being raised from  $0^\circ \text{C}$ . to  $4^\circ \text{C}$ .; it thus forms a *remarkable exception* to the general law that bodies expand by increase of temperature; above  $4^\circ \text{C}$ . water follows the general law of expansion and contraction by increments and decrements of temperature respectively, but between the limits  $0^\circ$  and  $4^\circ$  it behaves in exactly the opposite manner, *i.e.* it contracts for increments and expands for decrements of temperature—for on cooling from  $4^\circ$  to  $0^\circ$  it expands and regains its original volume. As the same weight of water occupies a less volume at  $4^\circ \text{C}$ . than at  $0^\circ \text{C}$ ., it follows that water is more dense at the former than at the latter temperature; and, since it obeys the general law of expansion for all temperatures between  $4^\circ \text{C}$ . and  $100^\circ \text{C}$ ., it is plain that water is most dense at the temperature  $4^\circ \text{C}$ . Water therefore, has a point of *maximum density*, and the temperature corresponding to its maximum density is  $4^\circ \text{C}$ . Hence, a given volume of water weighs more when measured off at  $4^\circ \text{C}$ . than when measured off at any other

\* This last molecule of water, being more firmly retained than the others, is termed *constituent water*.

temperature ; on the other hand, a given weight occupies a smaller volume at  $4^{\circ}$  C. than at any other temperature. Although the amount by which water contracts when heated from  $0^{\circ}$  C. to  $4^{\circ}$  C. is very small (a liter at  $0^{\circ}$  becomes .99988 of a liter at  $4^{\circ}$  C.), it still has a wonderful influence on the economy of Nature. It is by reason of this apparently trifling property that the waters of the temperate regions are not converted into ice by the cold of winter. 'In winter the temperature of lakes and rivers falls from being in contact with the cold air, and from other causes, such as radiation. The colder water sinks to the bottom, and a continual series of currents goes on until the whole has a temperature of  $4^{\circ}$  C. The cooling on the surface still continues, but the cooled layers, being lighter, remain on the surface, and ultimately freeze. The ice formed thus protects the water below, which remains at a temperature of  $4^{\circ}$  C., even in the most severe winters,—a temperature at which fishes and other inhabitants of the waters are not destroyed.'\*

The weight of a liter of water measured off at  $4^{\circ}$  C. is one kilogram = 1000 grams.

At  $62^{\circ}$  F. =  $16\frac{2}{3}^{\circ}$  C. an (English) imperial gallon of water weighs 10 lbs., or 70,000 grains, but a gallon filled with water at  $4^{\circ}$  C. ( $39\cdot2$  F.) contains 7 grains more, or weighs 70,007 grains.

When water is cooled down to  $0^{\circ}$  C. it begins to freeze, and at the same time to give out heat. The heat it evolves during solidification may be collected and measured by allowing it to be absorbed by other substances, the temperature of which is below the freezing point of water. The amount of heat given up by a kilogram of water at  $0^{\circ}$  in becoming ice is (as you are already aware) capable of raising the temperature of 80



kilograms of water from  $0^{\circ}$  to  $1^{\circ}$  C., or the latent heat of ice = 80 units. Other substances, also, evolve heat on passing from the liquid to the solid state. By a simple experiment this fact may be made manifest to the senses.

Here is a solution of Glauber's salt (sulphate of soda) ; it is hot, and is what chemists call a *saturated solution*, i.e. it contains as much of the salt in solution as the quantity of water is capable of dissolving at its present temperature. By allowing this to cool gradually while it is at rest (or undisturbed) it remains liquid, but if it then be poured over the bulb of a thermometer, the thermometer will exhibit a sudden rise of temperature, while a great portion of the solution will become solid. Water may be cooled down considerably below  $0^{\circ}$  C. *without becoming ice* by keeping it perfectly still, but if at all disturbed it suddenly becomes a mass of ice, and its temperature *instantly rises* to  $0^{\circ}$  C. It is a curious fact that water is specifically heavier in the liquid than in the solid state ; the weight of a cubic centimeter of water at  $4^{\circ}$  C. is 1 gram, while a cubic centimeter of ice weighs only .94 of a gram. Hence the specific gravity of ice (referred to water, at its maximum density, as unity) is .94.

As a consequence of its peculiar behaviour between the temperatures  $0^{\circ}$  C. and  $4^{\circ}$  C., water, while expanding in the act of freezing (i.e. in entering into the solid state), possesses enormous power ; by its sudden expansion it produces force sufficient to tear asunder the strongest materials, such as iron, stone, &c. <sup>100</sup> <sup>which</sup> <sup>that</sup> iron tubes used for water-pipes have, over and over again, been torn asunder by the water they contain, having been converted into ice. Rocks of all ages are year after year being split asunder from the rain water becoming frozen in their crevices.

Frost is thus one of the great agents to the action of which

the Geologist refers many important physical changes which our earth has undergone in the course of time.

As water in becoming ice gives out a *certain quantity* of heat, so ice in becoming water absorbs an *equivalent amount*; and for this reason the air feels warmer in frosty weather than during a thaw.

The freezing point of pure water, or rather the melting point of ice, is *constant*,—it never varies from  $0^{\circ}$  C.; it is, however, lowered by the presence of dissolved salts in the water. It is remarkable that no matter what salts may be dissolved in water, they separate, almost completely, from it when it becomes ice. Ice is, therefore, pure (solid) water. The presence of salts in solution has the effect of lowering the temperature corresponding to the maximum density. The point of maximum density of sea water, for example, is lower than that of fresh, and is even below  $0^{\circ}$  C.

I have said, before, that water obeys the ordinary laws of expansion and contraction between the temperatures  $4^{\circ}$  C. and  $100^{\circ}$  C. Let us now consider the effects of heat on it when at the temperature  $100^{\circ}$  C. When water is heated in an open vessel up to  $100^{\circ}$  C. (the barometer standing at 760 m.m.), it enters into *ebullition*, or, in other words, it begins to *boil*; if the heating action be now continued, the water gets no hotter, *i.e.* its temperature does not increase—a thermometer standing in the water still reads  $100^{\circ}$  C.; heat, however, is being imparted <sup>to</sup> the water, without affecting the thermometer. The <sup>heat</sup> thus imparted <sup>is</sup> termed *latent heat*; it is not true that it has no effect on the water, although it is *insensible* to the thermometer; for by its aid the water is gradually converted into steam, and the heat imparted, over and above that required to bring the water to boil, is stored up in the steam, from which it can be obtained back again by merely condensing the steam so formed into water at  $100^{\circ}$ .

A kilogram of water at  $100^{\circ}\text{C}$ . requires for its conversion into steam at the same temperature 537 thermal units, or degrees of heat. Hence the latent, or constituent, heat of steam is said to be 537.

If water be heated in an iron boiler provided with an escape pipe and safety valve, the steam being allowed to pass by the escape-pipe into a condenser exhausted of air—the steam thus escapes into empty space—and the valve be loaded with a weight equivalent to 1.0333 kilogram per square centimeter,\* the water will be found to *boil* when its temperature reaches  $100^{\circ}\text{C}$ ., that is, when the steam produced has sufficient elastic force (or *tension*) to lift the valve, and thereby escape through the pipe into the empty condenser.

By increasing the weight on the valve, the temperature at which the water enters into ebullition is increased too: thus, if the weight on the valve be doubled the water refuses to boil till its temperature is raised to  $120^{\circ}\text{C}$ .; and further, increase of pressure increases the temperature at which ebullition takes place, while, on the other hand, diminution of pressure diminishes the temperature of ebullition.†

Here is a flask of boiling water: I cork it well whilst it is still boiling, and by removing it from the source of heat I stop its ebullition. The flask now contains a small quantity of water, and the remainder of it is filled with the vapour of water. If now I condense vapour, by pouring cold water on neck of the flask (see Fig. 32), I will remove the pressure from the surface



Fig. 32.  
m.m.) is equivalent to  
ace.

\* The standard atmospheric pressure (760 m.m.) is equivalent to 1.0333 kilogram per square centimeter of surface thereon.  
† Advantage is taken of this fact in determining the heights of mountains by means of the boiling point of water.

of the water, which, you see, again boils, and even more briskly than before.

It is, therefore, evident that the temperature at which water boils is connected with the pressure on its surface.\*

As water may be made to boil at almost any required temperature, it is necessary to fix on some temperature as a standard; that chosen is the temperature corresponding to the ordinary pressure of the atmosphere at sea-level, viz. 760 m.m. of mercury. We may, therefore, define the boiling point of water as follows:—

*The boiling point of water is the temperature at which the elastic force, or tension, of its vapour is equal to the standard atmospheric pressure of 760 m.m. of mercury—or 1.0333 kilogram per square centimeter. The temperature at which the elastic force of the vapour of water is equivalent to the pressure 1.0333 kilogram per square centimeter has already been shown to be 100° C.*

Water, although most rapidly converted into vapour at the boiling point (the vapour is then called *steam*), gives off vapour at all temperatures above zero, and by making suitable arrangements for absorbing this vapour as fast as it is produced, *water may be frozen by its own evaporation.*† The vapour given off takes its constituent heat from the water, and the rapid abstraction of heat finally freezes it. Wollaston's Cryophorus and Carre's Ice Machine are well known arrangements for freezing water by evaporation.

An important property of water, which I had almost forgotten to mention, is its *great capacity for heat*. With the exception of *hydrogen*, its specific heat is higher than

\* Water boils when the elastic force of its vapour is equal to the pressure on its surface.

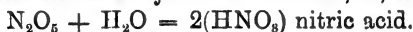
† When the elastic force, or tension, of the vapour of water is less than the pressure on its surface, vapour is given off only at the surface, and the process is then called *evaporation*.

that of any other known substance, or in other words (hydrogen excepted) it is more difficult to heat or to cool a given quantity of water than the same quantity of any other body. Water is, therefore, admirably adapted for cooking and other purposes where heat is required to be retained for a considerable length of time.

Water is a *neutral* oxide, *i.e.* it has neither acid nor basic action on litmus paper. It converts metallic oxides into hydrates, as—



while it transforms anhydrides into acids, as, for example,



Water probably unites *molecularly* with some bodies to form certain kinds of hydrated compounds termed *aquates*, such as the alums and other crystallized bodies containing water of crystallization.

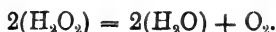
**Hydrogen Peroxide.**—Oxidised Water:—a remarkable substance known as peroxide of hydrogen, or *hydroxyl*, was discovered by Thenard in 1818: its molecule is represented by the formula  $\text{H}_2\text{O}_2$  or  $(\text{HO})_2$ ; and its semimolecule  $(\text{HO})$  is regarded as an important compound radicle.\* A dilute solution of hydroxyl may be prepared by passing a current of carbonic anhydride ( $\text{CO}_2$ ) through water containing barium peroxide† held in suspension.

\* The radicle  $\text{HO}$ , sometimes for convenience written  $\text{Ho}$  is an important *factor*, if I may so call it, in the molecular formulæ of many compounds, more especially so in the case of organic bodies, thus hydroxylamine ( $\text{NH}_2\text{HO}$ ) is regarded as ammonia in which one atom of hydrogen is replaced by the group hydroxyl  $\text{HO}$ .

† The barium peroxide is obtained by passing oxygen gas over barium oxide ( $\text{BaO}$ ) heated to redness in a porcelain tube.



The  $\text{H}_2\text{O}_2$  dissolves in the excess of water, and the solution is concentrated by evaporation over oil of vitriol into a syrupy liquid of peculiar odour. This liquid is readily decomposed into water and free oxygen; the decomposition takes place even at so low a temperature as  $20^\circ \text{C}.$ ; it is therefore not easily obtained in a warm climate.



Like chlorine it acts as a powerful bleaching agent; and like ozone it will oxidize the black sulphide of lead ( $\text{PbS}$ ) into white sulphate.



A solution of hydrogen peroxide is sold as a hair-wash; it has the effect of turning dark-coloured hair to a golden yellow hue.

Water possesses the power of dissolving many substances, solid, liquid and gaseous. The solvent power of water differs for different bodies; and a knowledge of the *degree of solubility* of bodies in water is of great value in the study of Analytical Chemistry. (See Table H. Chapter X.)

A pound of cold water will dissolve 2 lbs. of sugar or 2 ozs. of salt or 8 grains of lime. The solvent power generally increases with increase of temperature; thus boiling water will dissolve 16 times more saltpetre than ice-cold water; but as an exception to this rule, iced water dissolves twice as much lime as boiling water.

When the foreign matters dissolved in a water are present in sufficient quantity to impart a peculiar taste or smell, the water is called a *mineral water*. There are many varieties of mineral waters: the *saline*, as sea water and the water of saline springs; the *alkaline*, as the waters of Vichy; the *acidulous*, containing free carbonic acid; the *sulphurous*, containing sulphuretted hydrogen in solution as at Harrogate; the *chalybeate*, containing salts of iron in solution; and *siliceous*\*—waters.

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\* The Geysers of Iceland and New Zealand contain silica in solution.

Waters containing calcium and magnesium salts in solution are termed *hard waters*, and when such waters are used for washing purposes they waste a quantity of the soap before they allow it to produce a lather (or suds)—owing to the stearic acid of the soap forming *insoluble* stearates with the bases lime and magnesia.

Hard waters may be divided into two classes, namely, *temporarily hard* and *permanently hard* water.

Calcium carbonate ( $\text{CaCO}_3$ ) and Magnesium carbonate ( $\text{MgCO}_3$ ), held in solution by  $\text{CO}_2$  dissolved from the air, cause what is known as *temporary hardness*, as it may be removed by boiling. On boiling,  $\text{CO}_2$  gas is driven off, and then the originally dissolved calcium carbonate, becoming insoluble, precipitates. In this way the *fur* of kettles and *scale* in boilers are deposited.

Ordinary well-waters contain smaller quantities of mineral salts in solution than the true mineral waters. The nature of the salts contained in well-waters depends entirely on the nature and solubility of the constituents of the rocks in which the wells are sunk.

Wells in large towns or in the immediate neighbourhood of dunghills or cesspools are frequently contaminated by sewage, which, during slow oxidation is partly converted into nitrites and nitrates. Hence the presence of nitrites, or an abnormal proportion of saltpetre, in a water may be regarded as evidence of probable sewage contamination.

Temporary hard waters are now *softened* on a large scale in water reservoirs, &c., by the addition of *lime-water*,\* by which means the newly-formed lime carbonate is precipitated along with the carbonates (which were previously held in solution by the  $\text{CO}_2$ ) now precipitated with the added lime. This is known as Clark's process.

Waters are said to be *permanently hard* when they cannot be softened by boiling or by the addition of lime-water; such waters usually contain sulphates and chlorides of calcium and magnesium, &c.

The addition of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) has the effect of precipitating the earth bases contained in a hard water, while it replaces the salts of calcium and magnesium by corresponding salts of sodium, which do not waste the soap.

Very soft waters are capable of dissolving *lead hydrate*, which is

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\* Milk of lime is generally employed when large quantities of water have to be dealt with.

formed on the surface of lead pipes and cisterns exposed to the action of the air. Hence, lead salts being poisonous, it is unsafe to store soft water in lead cisterns, or to use lead pipes for its conveyance.

In mining districts salts of copper and arsenic are sometimes found occurring in the natural waters of the district.

Waters may, therefore, become so polluted as to be unfit for drinking and cooking purposes.

The amount of solid matters (chiefly salt) contained in *sea water* is, practically speaking, very constant at considerable distances from land surfaces. The average quantity of solids amounts to about 36 grams per liter of water—the relative density of sea water is 1.03.

The greater portion of the calcium and magnesium carbonates and silica thrown into the sea by rivers is used up by marine animals and plants in building up their shells and skeletons.



## CHAPTER XV.

### NITROGEN.

**N = 14; Density = 14.**

Nitrogen was discovered by Rutherford in 1772, in the atmosphere, as a substance incapable of supporting life or combustion. Chaptal called it *nitrogen*, in consequence of its being an element of *nitre*, and Lavoisier gave it the name *azote*\* from its inability to support respiration.

**Occurrence.**—It constitutes about four-fifths of the bulk of atmospheric air; occurs in saltpetre, or *nitre*, from whence it derives its name (*nitre-producer*), in coal, and as an essential ingredient in the tissues of all animals and of the generality of plants. So essential, indeed, is nitrogen to animal tissue that an animal has been (chemically) defined as ‘an *organic substance* which contains not less than *three per cent.* of nitrogen.’ Casein, albumen - blood and urea are highly nitrogenous substances formed in the bodies of animals fed on plants. Plants obtain their nitrogen from the soil and atmosphere.

**Preparation.**—Nitrogen may be separated from the oxygen with which it is mechanically mixed in atmospheric

\* From *a*, privative and ζωη (*zoe*) life; this name is still employed by the French.

air by causing the oxygen to combine with some substance, as phosphorus, for which it has a strong affinity. This is accomplished by enclosing, over water, a portion of air in a bell-shaped glass jar containing a stick of phosphorus suspended by a piece of copper wire. The phosphorus, gradually absorbing the oxygen of the air, undergoes *slow combustion*, and after the lapse of some hours all the oxygen present in the jar will have united with the phosphorus, producing by their union, in the presence of water, a compound known by the name phosphorus acid ( $\text{H}_3\text{PO}_3$ ), and leaving nitrogen in the jar.

Nitrogen is more rapidly insulated from the oxygen of the air by *igniting* a small piece of phosphorus on a metallic cup (standing over water) and covering it with a bell-jar full of air (Fig. 33). In this case the necessary initial temperature having been imparted to the phosphorus, *rapid combustion* ensues with the production of phosphoric anhydride, ( $\text{P}_2\text{O}_5$ ) which in the presence of water forms phosphoric acid ( $\text{H}_3\text{PO}_4$ ). By allowing the jar to stand in the water for some time, all the white fumes of phosphoric anhydride will be absorbed by the water, which will rise in the jar to fill the space originally occupied by the oxygen, leaving nitrogen in a tolerably pure state in the upper portion of the bell-jar. Its purity is increased by passing it through lime-water, by which means it loses the carbonic acid gas, which (being a constituent of the atmosphere) was present in the air from which the nitrogen was obtained. It may now be transferred into smaller jars for the purpose of examining its properties.



Fig. 33.

Another method of obtaining nitrogen from air consists in passing a stream of dry air over turnings of metallic

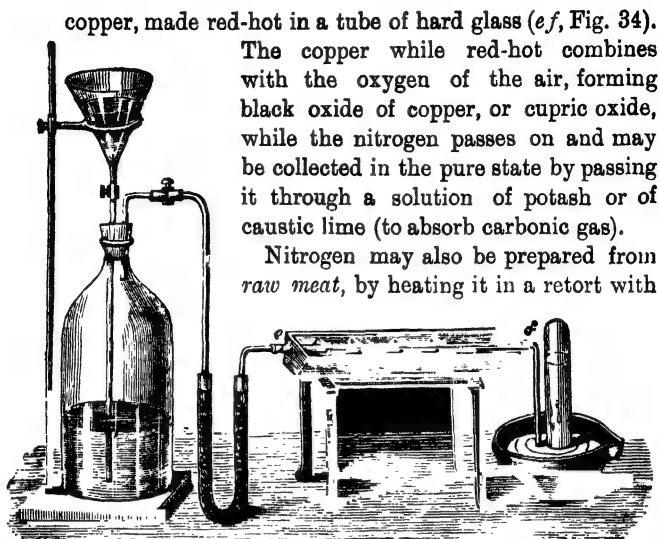
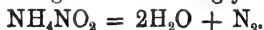


Fig. 34.

an acid. This process is more useful as a confirmation of the statement that *nitrogen is an essential ingredient of animal tissue* than as a means of preparing it, since it does not yield it free from impurities.

Nitrogen is also easily prepared by heating ammonium nitrite  $\text{NH}_4\text{NO}_2$  (or  $\text{NH}_3\text{HNO}_2$ ), which splits up into water and pure nitrogen when strongly heated, thus—



The ammonium nitrite may be readily prepared by heating a mixture of potassium nitrite and ammonium chloride.

Nitrogen is sometimes prepared by passing a stream of chlorine gas through a solution of ammonia; the process is dangerous, in consequence of the tendency to the formation of explosive oily drops, chloride of nitrogen ( $\text{NCl}_3$ ), and therefore not to be recommended to beginners.

Care should be taken to keep the ammonia in excess so as to avoid the production of the explosive chloride of nitrogen. The probable reaction is



**Properties.**—Here is a jar filled with nitrogen gas ; you observe that it is as colourless, tasteless and odourless as air. It is very sparingly soluble in water.\* Its chief characteristics are : its general inertness, and apparent want of affinity ; in fact an absence of positive qualities, *i.e.* it is better known by what it *does not* than by what it *does*. For example—it *does not* support combustion. For when I plunge this lighted taper into the jar it goes out, and moreover (you may notice) that the gas *does not* take fire, as hydrogen does, when a lighted taper is immersed in it. Nitrogen is, therefore, not only an extinguisher of ordinary combustion, but also (itself) *incombustible*. It *does not* give a milky appearance to lime water. It *does not* support respiration, for if a small animal be placed under a jar filled with nitrogen, it will die very quickly. An animal may be *drowned* in nitrogen gas as well as in water : for to be *drowned* in water is merely to die for want of free oxygen to oxygenate the blood ; and animals die in nitrogen, not from any poisonous action of the gas, but merely from its incapability of oxygenating the blood. Nitrogen is somewhat lighter than air, which is about fourteen and a half times as heavy as hydrogen. It has no action on litmus paper, and does not readily combine with other bodies. In fine, it may be said that nitrogen is most remarkable for its weak affinities for other elements. It requires the very highest temperatures to cause it to combine directly with oxygen.

With respect to the combustion of the ordinary

\* 100 volumes of water dissolve above 1.5 volumes of nitrogen gas.

materials used for fuel and illumination—coals, oils, candles, &c.—gases may be divided into three classes :—

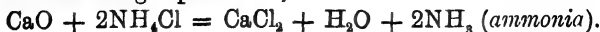
- (1) *Those which support combustion*,—well exemplified by oxygen.
- (2) *Those which do not support combustion, but are themselves combustible in air*,—exemplified by hydrogen.
- (3) *Those which neither support combustion nor are themselves combustible in air*,—exemplified by nitrogen.

Hence nitrogen (being the most abundant ingredient of the atmosphere) moderates the influence of the oxygen, or active agent, in the air we breathe.

Nitrogen—combined with hydrogen, and with hydrogen and oxygen, occurs in minute quantities in the atmosphere—combined with hydrogen as ammonia gas ( $\text{NH}_3$ ), and with hydrogen and oxygen as nitric acid ( $\text{HNO}_3$ ), two compounds which may be regarded as the primary sources of plant nitrogen. When flashes of fork lightning pass through moist air, nitric acid is produced, which can always be detected in the rain that falls during or immediately after thunderstorms.

The thunderstorms that usher in the Indian monsoons have, therefore, their beneficent, as well as their awe-inspiring aspects. Thus in many parts of India the soil from continued cropping, during thousands of years, has become so exhausted of its nitrogenous ingredients as to be entirely dependent on the monsoon for the acquisition of that *combined* nitrogen, necessary for the season's crop of cereals.

Ammonia was first prepared by the Arabs from camel's dung near the temple of Jupiter Ammon, whence it derives its name. This gas is now usually prepared by heating sal-ammoniac (ammonium chloride) with lime, the reaction being represented, thus :—



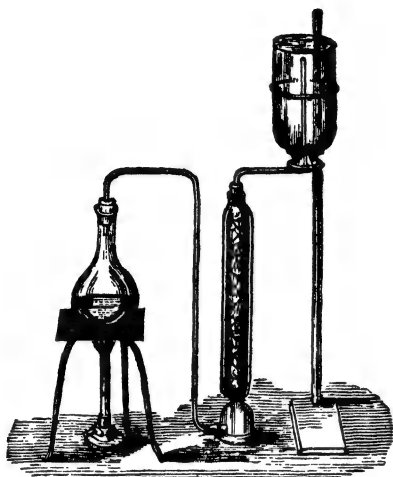


Fig. 35.

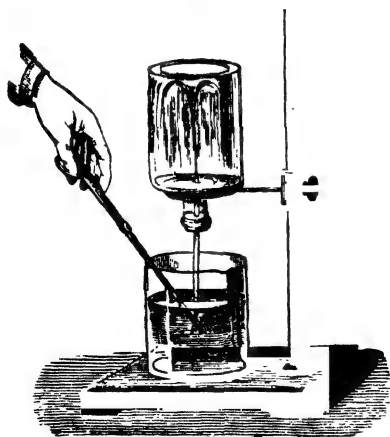
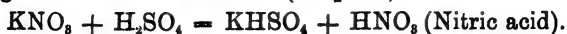


Fig. 36.

The accompanying figure represents the necessary apparatus. Even when mixed in the palm of the hand the pungent fumes of ammonia gas are readily perceived. The dry gas extinguishes a taper, but when mixed with highly-heated oxygen or a sufficiency of hot air, it takes fire and burns into nitric acid and water. This gas is extremely soluble in water, as may be illustrated as follows (see Fig. 36).

**Nitric Acid**, which also occurs in minute quantities in the atmosphere, is prepared for use in the arts by distilling oil of vitriol with nitre (saltpetre)—

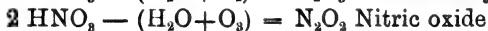


On the large scale Chili saltpetre, cubic nitre ( $\text{NaNO}_3$ ), is used instead of potassium nitrate, and by employing a higher temperature a smaller proportion of acid is required.

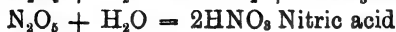
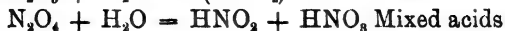
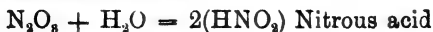


Nitric acid destroys the colour of a solution of indigo ; it dissolves copper, silver, mercury, lead, and zinc, &c., one or other of the lower *oxides of nitrogen* being at the same time evolved. It stains paper, wood, and skin yellow ; when mixed with  $\text{HCl}$  it dissolves gold ; it gives a characteristic reaction with  $\text{FeSO}_4 + \text{Aq}$ , forming a red liquid ( $2\text{FeSO}_4, \text{NO}$ ) which, if boiled, gives off nitric oxide, and the solution turns *brown*.

The relationship of these oxides to nitric acid may be symbolically exhibited as follows :—



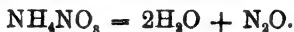
The three higher oxides are regarded as anhydrides, because they combine with water to produce acids—the *nitrous* and *nitric* acids.



As  $\text{N}_2\text{O}_4$  with water produces a mixture of both acids it goes by the name of *nitroso-nitric* anhydride ; it is also called the peroxide of nitrogen. The remaining two are

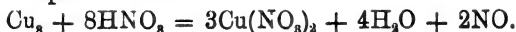
*neutral* oxides. They are known as *nitrous* oxide  $N_2O$  and *nitric* oxide  $N_2O_3$  or  $(NO)$ .\*

**Nitrous Oxide.**—This oxide is most easily obtained by heating ammonium nitrate ( $NH_4NO_3$ ) in a flask provided with a delivery tube and collecting the gas over hot water, it being rather soluble in cold water :



Here is a jar full of this gas ; it is colourless and odourless, its solution in water has rather a sweetish taste—it is liquefiable under pressure, and when the liquid is suddenly evaporated in vacuo a very low temperature is obtained. The gas, apparently, supports combustion well, but the feeble flame of burning sulphur is extinguished. It is, therefore, evident that the heat of the burning body decomposes the  $N_2O$  into its component gases before the combustion ensues. This gas is sometimes called ‘laughing gas’ because of its producing risible excitement when inhaled.

**Nitric Oxide** is usually prepared by bringing nitric acid into contact with strips of copper in a flask fitted with a delivery tube, when chemical action at once ensues even without the aid of heat. The action of the copper on the acid is represented thus—

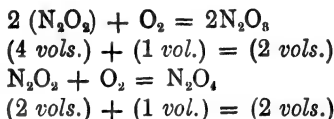


This gas is colourless, but on contact with free oxygen (or air) produces orange red fumes owing to its readiness to combine with oxygen in different proportions to form either  $N_2O_3$  or  $N_2O_4$ . The red fumes usually consist of a mixture of both these oxides. Nitric oxide thus becomes a convenient *test* for free oxygen. Like the monoxide it supports the combustion of such burning bodies as are *hot*

\*  $NO$  corresponds to a two gas volume molecule, but the ratio of constituent atoms is the same as in  $N_2O_3$ . For a similar reason  $O_4$  should be written  $NO_2$ .



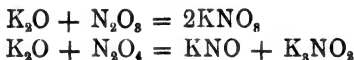
*enough* to decompose it beforehand. It has a neutral reaction before mixing with air or oxygen, by which it is converted into the acid forming bodies  $N_2O_3$  and  $N_2O_4$ . These latter oxides are obtainable by mixing together oxygen and nitric oxide in the necessary proportions as follows:—



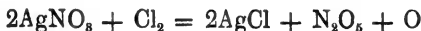
The peroxide  $N_2O_4$  is also prepared by strongly heating well dried lead nitrate—which is thus decomposed into lead oxide, nitric peroxide, and free oxygen.



Both of these oxides unite with bases to form salts—the former *nitrites* and the latter mixed *nitrates* and *nitrites*.



**Nitric anhydride** is insulated with great difficulty by acting on heated silver nitrate  $AgNO_3$  with dry chlorine gas—



it is an unstable, crystalline, white solid, which by contact with water, immediately forms nitric acid—



The *nitrates* are all soluble in water.

#### PHOSPHORUS P = 31.

The nitrogen group of elements comprises, besides nitrogen—

Phosphorus P	=	31
Arsenicum As	=	75
Antimony Sb	=	122
and Bismuth Bi	=	210

76 mean.

Of these Phosphorus (and perhaps Arsenicum)\* belongs to the non-metallic division of the elements.

Phosphorus occurs in nature as a constituent of various native phosphates, more particularly as calcium phosphate, which forms the principal ingredient in the minerals coprolite, phosphorite, apatite, &c. It is also an abundant constituent of the bones of animals. Phosphates occur among the constituent minerals of the primitive rocks, and hence also in the soils produced by their disintegration. Plants take up phosphorus from the soil in which they grow, and accumulate it in their seeds: hence science directs that the soil should receive phosphorus (in the shape of phosphates) as a special manure for seed-bearing plants such as the various kinds of corn (or cereals). And thus, the animal kingdom, by feeding on the vegetable kingdom, obtains the supplies of phosphorus necessary for its blood, bone and brain.

**Properties.**—Like oxygen and sulphur, phosphorus can exist in different allotropic modifications. Common (octohedral) phosphorus is a waxy-looking transparent solid, soft and flexible at ordinary temperatures, and possessing a slightly yellow tinge of colour. Phosphorus is a very inflammable substance, oxidising on exposure to the air, at first slowly, but increasing in rapidity of oxidation with increase of temperature. This is the cause of the luminous appearance it exhibits in a dark room, from which circumstance it derives its name ( $\phi\omega\varsigma$  light, and  $\phi\acute{\epsilon}\rho\omega$  I bear). In consequence of its great liability to oxidation it should always be kept under water even when manipulating with it.†

\* Arsenicum will be described with the metals.

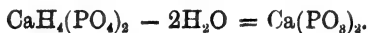
† If this precaution be not attended to, dangerous burns may result to the operator.

**Preparation.**—Phosphorus, though originally obtained from stale urine,\* is now always prepared from bones. The bones are first calcined; the white powder (called bone-ash) thus obtained is mixed with a sufficiency of dilute sulphuric acid (about two-thirds the weight of ash *plus* twice its bulk of water). The action of the acid on the bone-ash, which latter is chiefly composed of tri-calcic phosphate, may be represented as follows :—



The hydrogen of the oil of vitriol replaces part of the calcium in the tri-calcic phosphate, and thus forms the *acid phosphate* of calcium  $\text{CaH}_4(\text{PO}_4)_2$  known in commerce as superphosphate of lime.†

The solution of this acid phosphate is poured off from the precipitated calcium sulphate ( $\text{CaSO}_4$ ), and evaporated to dryness, after which the residue, being heated, to drive off water, is transformed into calcium metaphosphate ( $\text{CaPO}_3$ )<sub>2</sub>.



This metaphosphate is finally mixed with powdered charcoal and heated strongly in an earthenware retort, to which a copper tube is attached, by which the vapour of the phosphorus, which distils over, is conducted into a vessel containing cold water. The reaction is represented as follows :—

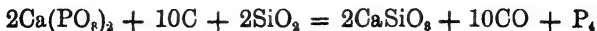


In this way one-third of the phosphorus is still left behind as tri-calcium phosphate. The whole of the

\* The urine voided by a man in 24 hours contains on an average about 3 grains of phosphoric acid. The urine of brain-workers contains much more phosphoric acid than that of mere physical labourers. Hence a phosphatic diet is sometimes prescribed for brain-workers.

† Owing to its ready solubility this superphosphate forms a highly-valued manure, especially for root crops and pastures.

phosphorus, however, may be obtained by adding a sufficiency of sand (silex,  $\text{SiO}_2$ ) to the mixture in the retort, when the reaction becomes—



The phosphorus is condensed in waxy-looking drops at the bottom of the water. By heating the water, the phosphorus melts, and it is then run (through wash-leather) into glass or copper moulds, forming sticks, such as may be purchased at any druggist's shop.

**Uses.**—Phosphorus is used principally for making lucifer matches, and also for the preparation of phosphoric acid and in medicine. For the manufacture of matches red (amorphous) phosphorus is now universally used. The red modification of phosphorus is obtained by the prolonged heating of ordinary white phosphorus at temperatures from  $230^\circ$  to  $250^\circ \text{C}$ .,—taking precautions to exclude the air while being heated. Unlike ordinary phosphorus it may be handled with impunity; and it is insoluble in carbon disulphide, turpentine, and oil, liquids in which the common variety more or less readily dissolves.

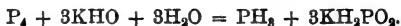
The fumes of phosphorus are very poisonous and are very deleterious to the health of persons engaged in the match trade: but with the introduction of amorphous red phosphorus, the match manufacturer has gained a new lease of life. Matches are now made which 'ignite only on the box'; such matches are usually tipped with molten sulphur or paraffin, and then dipped in a paste composed of a mixture of potassium chlorate (6 parts), antimony sulphide (2 parts), and glue (1 part).

Red phosphorus (10 parts) and antimony sulphide (8 parts) are ground up with a sufficiency of glue, and spread

on paper, which is pasted on the side of the box to form the friction surface.

A thousand tons of phosphorus are annually used in the manufacture of matches, and thus the soil is deprived of a large quantity of phosphoric acid and, perhaps, mankind of some brains.

**Phosphuretted Hydrogen.**—A remarkable compound of phosphorus and hydrogen, called *phosphine* or *phosphuretted hydrogen*, is a basic body perfectly analogous to the ammonia type ( $\text{NH}_3$ ). It is obtained by heating a solution of caustic potash on phosphorus—

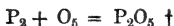


Corresponding chlorides, bromides and iodides also exist or can be made.

Phosphuretted hydrogen has an offensive, garlic-like odour, and inflames on passing into the air, producing fumes of phosphoric anhydride ( $2\text{H}_3\text{P} + \text{O}_5 = \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$ ) which rise in pretty rotating rings, resembling *gunner's rings* frequently to be observed during the firing of cannon. The spontaneous inflammability of this gas is probably due to the presence of a trace of the vapour of *liquid phosphuretted hydrogen*—another compound of phosphorus and hydrogen represented by the formula  $\text{P}_2\text{H}_4$ . This liquid compound, on exposure to direct sunshine, deposits a yellow *solid* which is a third compound of these elements having the constitution  $\text{P}_4\text{H}_2$ —



**Phosphoric Anhydride** ( $\text{P}_2\text{O}_5$ ) is a white snow-like solid with a great affinity for water,\* with which it combines in several proportions according to the circumstances under which these bodies are brought together. It is prepared by burning phosphorus in dried air or oxygen.



\* It is consequently much used for drying gases, for which purposes it equals strong sulphuric acid.

† With an excess of phosphorus, low temperature and an insufficient supply of air a lower oxide  $\text{P}_2\text{O}_3$  is formed; this, by combining with water, forms phosphorous acid ( $\text{H}_3\text{PO}_3$ ), which on being strongly heated, breaks up into phosphuretted hydrogen and orthophosphoric acid.

When the solid anhydride is thrown into water it hisses violently while entering into combination with the water. It forms *three* distinct *hydrates* by combining with different proportions of water, and these are known as varieties of phosphoric acid.

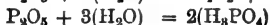
**Phosphoric Acid.**—The three varieties of phosphoric acid are :—

Meta-phosphoric acid  $\text{HPO}_3$

Pyro-phosphoric acid  $\text{H}_4\text{P}_2\text{O}_7$

Ortho-phosphoric acid  $\text{H}_3\text{PO}_4$

and, theoretically speaking, they may be regarded as formed by the combination of phosphoric anhydride ( $\text{P}_2\text{O}_5$ ) with successive molecules of water. Thus :—



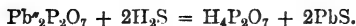
Thus it appears that *metaphosphoric acid* is *monobasic*, *pyrophosphoric acid* *tetrabasic*, while *orthophosphoric acid* (the ordinary acid met with in combination with bones, &c.) is *tribasic*.

*Orthophosphoric acid* is the only really stable compound of the three; for solutions of meta- and pyro-phosphoric acids are converted into the ortho-acid on boiling with a sufficiency of water; even the cold solutions undergo a similar change on keeping for some time. The ortho-acid can be obtained by the action of dilute nitric acid on phosphorus—



*Metaphosphoric acid* is obtained by dissolving in small quantities of water the freshly-prepared phosphoric anhydride, obtained by burning phosphorus in air or oxygen. If the solution thus obtained be boiled for some time with excess of water, the metaphosphoric becomes converted into orthophosphoric acid.

*Pyrophosphoric acid* can be obtained, as its name implies,\* by heating ordinary phosphoric acid to  $220^\circ \text{C}$ . It is more commonly prepared by decomposing the pyrophosphate of lead with sulphuretted hydrogen :—



These three varieties of phosphoric acid can readily be distinguished from one another by their peculiar behaviour with silver

---

\* From *pyr*, *fire*.

nitrate and albumen (white of egg). A solution of metaphosphoric acid *coagulates* albumen and gives a *white* precipitate with nitrate of silver. Pyrophosphoric acid does not coagulate albumen, and gives no *white* precipitate with silver nitrate (unless neutralised).

Orthophosphoric acid does not coagulate albumen, and it gives a *yellow* precipitate with nitrate of silver solution.

### *Familiar Nitrates.*

Hydric nitrate .....	Nitric acid.....	$\text{HNO}_3$
Sodic nitrate .....	Cubic nitre, Chili salt-petre	$\text{NaNO}_3$
Potassic nitrate .....	Nitre, Saltpetre, Sal prunella, Bengal salt-petre	$\text{KNO}_3$
Ammonic nitrate .....	.....	$\text{AmNO}_3$
Argentio nitrate .....	Lunar caustic .....	$\text{AgNO}_3$

### *Familiar Phosphates.*

Monosodium phosphate	Acid phosphate of sodium	$\text{NaH}_2\text{PO}_4$
Common sodic phosphate	Hydric disodic phosphate (Neutral phosphate)	$\text{Na}_2\text{HPO}_4$
Trisodic phosphate ....	Basic phosphate .....	$\text{Na}_3\text{PO}_4$
Sodium ammonium } Hydrogen phosphate }	Microcosmic salt .....	$\text{NaNH}_4\text{HPO}_4$
Silver phosphate .....	Yellow phosphate of silver	$\text{Ag}_3\text{PO}_4$
Silver metaphosphate ..	White phosphate of silver	$\text{AgPO}_3$
Magnesium ammonium phosphate.	.....	$\text{MgNH}_4\text{PO}_4$
Tricalcium phosphate..	.....	$\text{Ca}_3(\text{PO}_4)_2$
Monocalcium phosphate	Superphosphate of lime	$\text{CaH}_4(\text{PO}_4)_2$

## CHAPTER XVI.

### CARBON.

Tetrad, C<sup>iv</sup> = 12.

Carbon, in combination with oxygen, enters the atmosphere as a result of the action of animal life: it will therefore be necessary to know something of carbon and its oxides before we commence to discuss the chemistry of air more fully.

**Occurrence.**—Three varieties of carbon occur free, or uncombined, in Nature. These varieties are known by the names *Diamond*, *Plumbago*, and *Anthracite*, or coal.

It occurs, however, most abundantly in a state of combination with oxygen and with hydrogen. With oxygen it forms carbonic anhydride, which is found in the atmosphere, and which forms 44 per cent. of all pure limestones, chalk, marble, corals, &c. In union with hydrogen it forms the main constituent of bituminous coal; it is also an essential ingredient of plants and animals.

Each of the three native forms of carbon is characterized by properties peculiar to itself.

*Diamonds* are usually found as transparent crystals, which are generally destitute of colour; sometimes, however, they are covered with a thin opaque crust.

The density of the diamond, referred to water as unity, is about 3.5. The diamond is the *hardest* known substance, and for this reason is used for cutting glass and (in powder) for cutting and polishing the gem itself.



With one exception,\* it possesses a higher power of refracting light than any other body. It has also a most brilliant lustre. It is a bad conductor of heat and electricity. It is combustible in oxygen with the production of *carbonic anhydride* (carbonic acid gas), a property which is *common to all varieties* of carbon.

The diamond is chiefly used as a personal ornament, and for this purpose it is cut by lapidaries into shapes, which are known by the names *rose* and *brilliant*. The *rose* is flat below, and is cut above so as to exhibit 24 facets. The form of the *brilliant* is the same, but it is domed below as well as above, and is similarly cut on the two surfaces. When cut and polished a diamond weighing 1 carat† is valued at about £8, and its *price augments as the square of its weight* until this latter reaches about 20 carats; above this weight its price rises in a much quicker ratio. Diamonds are generally found in the alluvial *débris* of the primitive stratified rocks.

Diamonds come mostly from Borneo, Brazil, and Cape Colony. In this country (India) they are found in a sandstone known as the *diamond sandstone*, which occurs in the southern parts, chiefly between Masulipatam and Hyderabad, where the celebrated *Kohinoor* was discovered.

“The Kohinoor, or ‘Mountain of Light,’ became the property of the Queen of England on the annexation of the Punjab in 1850. It is reputed to be 4,000 years old, and it is certain that in 50 B.C. it belonged to the Rajah of Ujayin, and remained in the possession of his successors until the Mahomedans conquered India. The Kohinoor is mentioned by Tavernier, A.D. 1665, as the property of the Great Mogul.

\* Lead chromate.

† 1 Carat =  $3\frac{1}{8}$  grains.

Its original weight was 703 carats, and it has been reduced by repeated cuttings to its present weight, which is only  $103\frac{1}{2}$  carats. It is thought that the original rough form of the Kohinoor was that of a *rhombic dodecahedron*, and that this great mass was broken accidentally into three parts, forming the *Kohinoor*, the *Russian diamond*, and the *Dorianoor* or '*Ocean of Light*.' The Russian diamond weighed 194 carats, and was sold for £90,000 and an annuity of £4,000. The Kohinoor and Dorianoor formed part of the plunder seized by Nadir Shah at the taking of Delhi in 1739, when the treasures carried off exceeded £70,000,000 in value."\*

*Plumbago* (called *graphite* from being used for writing purposes) is found native in several parts of the world, but the best kind comes from Borrowdale in Cumberland, where it occurs in trap rock. Its colour varies from black to iron-grey; it has a metallic lustre, and makes a black mark on paper, and under the erroneous name of *black-lead*† is used for making pencils; the coarse kinds are used for polishing stoves, &c., and (in powder) for diminishing friction between the parts of machines. It contains a trace of iron, in combination with some of its carbon as carbide of iron, and is therefore not so pure as the diamond, which is almost free from any impurity. Indeed, were it not for the fact that both combine with oxygen to produce the *same compound* (carbonic anhydride) it would be difficult to believe that the diamond and plumbago are one and the same substance. Unlike the diamond, however, it is a good conductor of heat and electricity.

*Anthracite* is a variety of coal which contains no *bitumen* (an inflammable material chiefly composed of

\* Houghton, 'Kingdoms of Nature.'

† The name is erroneous, as plumbago contains no lead whatever.

of which gives to animal charcoal a greater power of removing the colouring matter from liquids than is possessed by ordinary wood charcoal; this variety is consequently used for such purposes by sugar refiners. This property of animal charcoal may be well illustrated by throwing some of it into the blue liquid you see in this glass (water coloured blue by sulphate of indigo) and filtering it, to separate the liquid portion from the solid charcoal. You observe that the *filtrate* (*i.e.* what passes through the filter) is perfectly colourless, like water.

Animal charcoal being made from bones is frequently called *bone-black* and *ivory-black* (having been originally made from ivory).

Another variety of charcoal is well known as *lamp-black*: it is obtained by burning *hydrocarbons* (as turpentine, rosin, &c.); it is also deposited from the smoke of *lamp flames*, hence its name. Lamp-black is used as a *paint*, and when mixed with soap and linseed oil forms *printing ink*.

*Soot* is an impure variety of carbon resembling lamp-black.

Charcoal is commonly thought to be *antiseptic* (that is, possessed of properties which prevent decay), in proof of which it is stated that water may be kept in drinkable order for a long time in wooden vessels which have been charred on the inside, and that meat may be kept sweet for a considerable time by covering it with powdered charcoal. Although such statements be perfectly true, yet the manner in which charcoal acts is quite the *opposite* to that which is popularly supposed: for these effects are due to the *power of absorbing gases* which charcoal possesses in a high degree. A given volume of charcoal absorbs about nine times its bulk of oxygen gas; and, thus condensed, oxygen has a very powerful affinity

for the *decaying organic matter* occurring in stagnant waters and putrid meat. The effects (those just mentioned) of charcoal on water and meat are caused by the *oxidating action* of the absorbed oxygen, which, combining with the odoriferous organic matter, renders it harmless by resolving it into carbon dioxide and water. The decomposition is, therefore, *hastened* instead of *retarded*, as is implied by the term antiseptic.

According to experiments conducted by Saussure, at the ordinary atmospheric temperature and pressure :—

1 vol. of boxwood charcoal absorbs 90 vols. of Ammonia.	
85	„ Hydrochloric acid.
65	Sulphur dioxide.
55	Hydric sulphide.
35	Carbon dioxide.
9	Oxygen.

Cocoanut charcoal absorbs considerably more than that made from boxwood ; according to Hunter one volume of cocoanut charcoal absorbs eighteen volumes of oxygen.

The absorbed gases are evolved when the charcoal is heated. *Charcoal filters are, therefore, easily cleansed by giving the charcoal a red heat.*

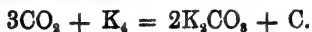
Heaps of charcoal occasionally take fire *spontaneously* ; such a phenomenon being most probably caused by the slow combustion of the carbon with the oxygen condensed in its pores. The condensation of the gas probably producing (as in the case of spongy platinum) *sufficient heat to start the combination* by a slow process, which finally yields the necessary amount of heat for their rapid combustion.

Charcoal, like hydrogen, is *capable of reducing* metallic oxides, and is often employed for that purpose. Carbon unites directly with oxygen ; you have seen it do so with brilliant combustion on a former occasion, when I

plunged a reddened piece of it into a jar of oxygen, the product being carbon-dioxide—



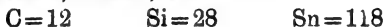
The combustion of the diamond, graphite or charcoal, in oxygen, yields this compound, and for every 12 grams of pure carbon so burned, 44 grams of carbon-dioxide are produced, with the development of 97 units of heat.\* Carbon is partly liberated from its combination with the oxygen in carbonic anhydride by contact with ignited potassium or sodium—



As carbon has never been *volatilized*, its experimental vapour-density has not been ascertained.

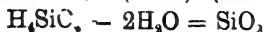
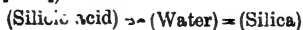
#### SILICON. Si = 28.

Silicon is the only other non-metallic element belonging to the tetrad (or carbon) group of elements. This group contains Carbon, Silicon, and Tin—



**Occurrence.**—Silicon, though next to oxygen the most abundant constituent of the earth's crust, is not found free in nature. It always occurs in combination with oxygen, chiefly as silicon-dioxide, or silica ( $\text{SiO}_2$ ). This substance ( $\text{SiO}_2$ ) when it occurs in the crystalline condition is called *quartz*, rock crystal, &c. ; and when in the amorphous condition it is known as *calcedony*, flint, &c. Many of the precious stones, as *amethyst*, *agate*, *carnelian*, *onyx*, &c., are composed of silica ; *opal* is a hydrated form of silica.

Silica, or Silicon-dioxide, is really the anhydride of—  
*Silicic acid* ( $\text{H}_4\text{SiO}_4$ ) :—for



\* A kilogram of carbon when burnt completely in oxygen yields 8,080 units of heat.

and when combined with bases it forms the largest and most important class of minerals—the *Silicates*—which enter into the composition of rock formations. Even ordinary clay is a more or less pure silicate,—pure clay (or kaolin) is silicate of alumina ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2, 2\text{H}_2\text{O}$ ), and therefore bricks, pottery, china and glass, which are composed chiefly of clay and sand, also come under the head of silicates.

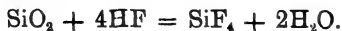
**Preparation.**—Silicon itself can be obtained in the two conditions, amorphous and crystalline ; it is, however, seldom prepared (except for curiosity), as it serves no useful purpose in the Arts. The amorphous variety may be prepared, as a dull brown powder, by fusing potassium silico-fluoride ( $\text{K}_2\text{SiF}_6$ ) with either of the alkali metals, potassium or sodium—



*Crystalline* silicon is obtained in lustrous black hexagonal plates by fusing the silico-fluoride ( $\text{K}_2\text{SiF}_6$ ) with the metal aluminum, and afterwards dissolving out the metallic aluminum with hydrochloric acid.

**Properties.**—Amorphous silicon is combustible in air or oxygen, forming the dioxide ( $\text{SiO}_2$ ), usually termed silica.

The most remarkable property of silicon, as well as of its oxide silica, is the power of resisting the action of all acids except that of hydrofluoric ( $\text{HF}$ ), and this acid converts it into the gaseous body ( $\text{SiF}_4$ ), tetra-fluoride of silicon. This action of hydrofluoric acid on silica is represented thus—



It explains how  $\text{HF}$  acts on glass vessels by flying away with the silicon of the glass as  $\text{SiF}_4$ .

This gaseous body,  $\text{SiF}_4$ , when conducted into water undergoes a reaction with the water by which silica is

separated in a *gelatinous* condition, while a solution of Hydro-fluosilicic acid is left in the water. The *jelly* is composed of silicic acid.



This acid ( $\text{H}_2\text{SiF}_6$ ) in solution is frequently used in analysis to distinguish between soluble compounds of potassium and sodium, as it gives a glairy gelatinous precipitate with the former, but not with the latter class of compounds.

The barium salt is insoluble in water and dilute acids ; and for this reason fluo-silicic is liable to be mistaken for sulphuric acid. Silico-fluorides are, however, easily distinguished from sulphates by the readiness with which they yield hydrofluoric acid (which etches glass) when treated with strong oil of vitriol, thus—



From a solution of the silicates of potash or soda (water glass) gelatinous silica is precipitated on the addition of a strong acid ( $\text{HCl}$ ,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ).



### BORON. B = 11.

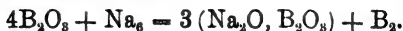
Boron is an element of peculiar analogies ; for though a *triad*, and therefore not properly belonging to the carbon group, it bears such striking resemblances to silicon and carbon that it is best considered in conjunction with these elements.

**Occurrence.**—Like silicon, boron is nowhere found free in nature, it occurs only in combination, and chiefly with oxygen and sodium as boric (boracic) acid, and as borax (tincal) ; the former is found in the hot water lagoons of Tuscany, and the latter occurs in Thibet as an efflorescence on the soil. Boron also occurs in minute quantity in some rare minerals, such as tourmaline, &c.

**Preparation.**—Boron is obtained by a process exactly similar to that adopted in the preparation of silicon: boro-fluoride of potassium is fused with metallic potassium—



It may also be prepared by igniting boric anhydride ( $\text{B}_2\text{O}_3$ ) with sodium, thus—



**Properties.**—Thus prepared, boron is an amorphous olive brown powder which soils the fingers, but like silicon it assumes the crystalline condition when fused with aluminum. Boron also assumes a condition known as *graphitoidal*, i.e. resembling the lustrous scales of graphite. Graphitoid boron is obtained by passing the terchloride of boron ( $\text{BCl}_3$ ) over fused aluminum—



The boron dissolves in the excess of aluminum, which is itself subsequently dissolved out by caustic soda. The only important compounds of boron are boric, or boracic, acid ( $\text{H}_3\text{BO}_3$ ) and borax ( $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$ ), both of which compounds are much used in blowpipe experiments. Compounds of boron impart a peculiar *green* colouration to the flame of a spirit lamp. Boracic acid solution gives a brownish red colour to yellow turmeric paper, after drying. Borax, owing to its great power of dissolving metallic oxides at high temperatures, is much used for cleaning the surfaces of metals in the art of soldering, and for making artificial gems before the blowpipe.

Boron forms a gaseous compound with Hydrogen ( $\text{BH}_3$ ) of similar constitution to ammonia ( $\text{NH}_3$ ) and phosphuretted hydrogen ( $\text{PH}_3$ ), which is strong evidence in favour of viewing Boron as a member of the nitrogen group of elements.



## CHAPTER XVII.

### THE OXIDES OF CARBON.

Carbon forms only two compounds with oxygen: they are *carbon-dioxide* or carbonic anhydride (commonly called carbonic acid gas)  $\text{CO}_2$ , and *carbon-monoxide*, or carbonic oxide,  $\text{CO}$ .

#### CARBON-DIOXIDE.\*

Molecule,  $\text{CO}_2 = 44$ ; Density = 22.

**Occurrence.**—In the free state it occurs in the atmosphere, being evolved from volcanoes, from the lungs of animals during respiration, and from the combustion of fuel; it is also evolved from plants during the night. In combination with lime it forms (as already mentioned) upwards of 40 per cent. of limestone, marble, corals and the shells of marine animals.

**Preparation.**—It is most easily obtained from calcium carbonate, in which it may be said to exist ready made, by the action of hydrochloric or sulphuric acid.

The materials generally used in the laboratory are white marble or chalk and hydrogen chloride (hydrochloric acid). The marble or chalk is put into a gas-generating bottle (Fig. 37) with some water, and strong hydrogen chloride is dropped in occasionally, so as to keep up a brisk disengagement of the gas; it is best collected by upward displacement of air, *i.e.* by bringing the end of the delivery tube to the bottom of a gas jar or bottle, and

\* The dioxide, commonly called 'carbonic acid gas,' being a natural compound, we shall begin with it.

covering it loosely with a card; the carbon-dioxide being heavier than air falls to the bottom, and displaces the air *upwards*.

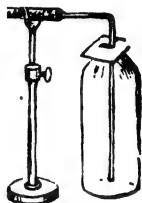


Fig. 37.

The action of hydrogen chloride on calcium carbonate is represented thus—



The products are calcium chloride ( $\text{CaCl}_2$ ), water ( $\text{H}_2\text{O}$ ), and carbonic anhydride ( $\text{CO}_2$ ). It may be freed from watery vapour by causing it to pass through a tube packed with fragments of quicklime or other desiccating substance. When required for making soda-water it is usually prepared from chalk and hydrogen sulphate (sulphuric acid) diluted with a'out ten times its bulk of water. Any carbonate will part with its carbonic acid gas when brought into contact with a strong acid\*—such as hydrochloric, sulphuric, or nitric.

Having filled a few bottles with the gas, we may proceed to examine its properties.

**Properties.**—Carbon-dioxide, or carbonic anhydride, is a gas devoid of colour, and hence as invisible as air. It pos-

\* Hence when effervescence takes place on the addition of an acid it generally indicates a carbonate, unless the escaping gas emits a peculiar odour.

sesses other properties, however, by which it may be readily distinguished from air. The following are its principal characteristic properties :—

*It extinguishes a lighted taper :* you will observe, when I immerse a lighted taper in a bottle full of it, that the taper will be immediately extinguished.

*It is very dense, being about 1.52 times as heavy as air.* This property may be demonstrated by pouring some of the gas over an ignited taper. I take a jar full of this gas, and pour it (as I would water) down on the wick of the taper ; you see I have now done so, for the taper is extinguished ; or, I may take another jar of the gas and empty its contents—carbonic acid gas—into a jar (Fig. 38) containing air only. In this case the carbon dioxide falls through the air into the jar, at the same time displacing (upwards) the air from the jar. That it really has been poured into this jar I will now prove to you. Here is a lighted taper, and if there be carbonic anhydride in this jar (the one which just now contained air only) the taper will be extinguished when I plunge it into it. There ! you see the taper goes out. I may further illustrate the great density of carbonic anhydride by floating a small balloon or soap-bubble on its surface in a large jar.

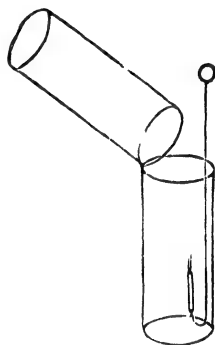


Fig. 38.

*It is soluble in water to the extent of one volume of the gas to one volume of water,* and in common with other gases, it is absorbed in the same ratio when in a compressed state ; it imparts an agreeable *sharp* or *acid*

*taste* to water, well-known to those who drink soda or other aerated waters.

When dissolved in water it *reddens* (slightly) *blue litmus paper*, and moistened blue litmus paper is reddened (wine-red) when introduced into a jar of the dry gas; the blue colour of the paper is restored when its moisture is evaporated. Carbonic anhydride, therefore, becomes an *acid* when dissolved in water\*; the formula assigned to a solution of it in water is—



*It imparts to clear lime-water a milky appearance.* This is caused by the carbon dioxide entering into combination with the lime, thereby producing calcium carbonate or chalk (the same substance from which it was liberated in the first instance by the action of an acid), which is *insoluble* in water, and hence gives it a milky appearance; if allowed to stand for a time, the solid carbonate of calcium will fall to the bottom, and leave the water clear above. This property is shown thus:—Here is a jar of the gas, and here some lime-water, which I now pour into the gas, and, covering the jar with a glass plate (Fig. 39), I shake it up, gently first, and afterwards rather briskly. You see now the water presents a milky appearance. This lime-water is the common test for, or witness to, the presence of carbon-dioxide.



Fig. 39.

*It does not support animal respiration.* A mouse or other small animal, introduced into a jar of it, dies almost immediately.

Carbon-dioxide does not extinguish the flame of a taper

\* This fact accounts for the name *carbonic acid gas* which is so frequently applied to this compound.

for the same reason that hydrogen and nitrogen do, *i.e.* by excluding oxygen, for carbon-dioxide itself contains a large quantity of *combined* oxygen, and even when mixed with a good share of *free* oxygen it (carbon-dioxide) will extinguish the flame of a taper. It exerts a *poisonous action*, so to speak, on combustion, similar to its action on animal life.\* Thus from 4 to 6 per cent. of carbonic anhydride in air is sufficient to poison (or extinguish) animal life, and, as we would naturally expect, a larger percentage is required to extinguish the flame (or life) of a candle, which is produced by *rapid combustion*; if the air contained 14 per cent. of carbonic anhydride, a candle would cease to burn in it.

If we were to make an artificial atmosphere with carbon-dioxide, and the same quantity of free oxygen as is found in the natural one, in which man can live and candles burn with facility, the life of a man, as well as that of a candle, would be an impossibility. I shall now make a specimen of such an atmosphere, and show you that it will extinguish a lighted candle or taper, and therefore would also extinguish your lives—do not look frightened, as I am not going to experiment on any of you.

For this purpose I mix together (by transference over the pneumatic trough) four volumes of carbonic anhydride and one volume of oxygen. Here is the mixture, and if I now plunge a lighted taper or candle into it you will see it go out. There, it's gone! Carbonic anhydride is, consequently, said to be neither a *combustible* nor a *supporter* of combustion; and though this statement be true with reference to the ordinary materials used for fuel and illumination (coals, candles, &c.), yet it is *not*

\* The process by which animal respiration (on which life depends) is carried on is a kind of *slow combustion*—*i.e.* combustion without light, and is called *eremacausis*.

*absolutely* true, as may be experimentally demonstrated as follows:—

Here is some of the metal magnesium in the form of a ribbon. I take a piece of this and fasten it to a cork which exactly fits this large deflagrating jar, full of carbonic anhydride. Now holding this piece of ribbon magnesium in the flame of a lamp till it begins to burn brightly, I then plunge it into the jar of gas ; you will now observe that the carbon-dioxide *supports the combustion* of magnesium wire, which burns most brilliantly in it—with the production of (those white flakes) oxide of magnesium, carbon at the same time being separated, or set free, as a consequence of oxygen which was originally combined with the carbon having left it for the magnesium. Those black particles you see are carbon : they may be collected by adding to the oxide of magnesium water, acidulating the mixture with hydrochloric acid and filtering ; the carbon, being an insoluble body, is left on the filter.

Hydrogen, too, has been called an extinguisher of combustion, still a jet of oxygen may be burned in an atmosphere of hydrogen.

We may, therefore, conclude that *combustion is a phenomenon which results from the chemical action of one substance upon another*, and this, we know, is always accompanied with the evolution of heat, and frequently of light.

Carbonic anhydride is evolved during the respiration of animals in large quantities. About 4 per cent. of the air we exhale consists of carbonic anhydride. I will now show you that expired air contains carbonic anhydride. As lime-water is the common test for this gas, if I pass some expired air through lime-water by means of a tube (*exhaling* the air that has done its work in my lungs through the tube, and *inhaling* fresh air through my nose) the clear lime-water

ought to become milky if the exhaled air contain carbonic anhydride—wait a bit—there it is ! You observe that the liquid which was quite clear and sparkling a minute ago, has now a milky appearance, owing to the formation of an insoluble fine white mud,—*precipitated calcium carbonate* ( $\text{CaCO}_3$ )—which proves that carbonic anhydride is present in the air which escapes from my lungs during respiration: and the same is true of you and of all breathing animals.

Let us now try what effect an *additional quantity* of carbonic anhydride will have on the calcium carbonate formed in the last experiment. Continuing to pass carbon-dioxide (from the generating bottle) through the *now* turbid liquid, for some time after all the calcium has been precipitated as carbonate, I restore the liquid to its original clear and sparkling condition. The precipitated calcium carbonate is *dissolved* by the excess of carbon-dioxide, which converts the *insoluble\** carbonate into a *soluble* salt called *hydro-calcium carbonate*, also named *bicarbonate of calcium*. If, now, I heat this clear solution, it again becomes *turbid* owing to the *added* carbon-dioxide evaporating with the water,—the *insoluble* carbonate being again left behind. Water impregnated with carbonic acid gas dissolves the *insoluble* carbonate, and this *dissolved* carbonate is found in the waters of all limestone districts. During ebullition the excess of carbon-dioxide is driven off, and there is left the insoluble carbonate which forms those troublesome incrustations so often found in boilers and kettles. Even by exposure to sunshine the excess of carbon-dioxide is evaporated, and consequently the *soluble* becomes converted into the *insoluble* (crystallized) carbonate of calcium. This process

\* The term insoluble without qualification means insoluble in water alone.

is continually taking place in Nature wherever streams of water containing the dissolved carbonate are exposed to the air, the deposit being called *Calcareous Tufa* when it occurs as a porous mass with cellular structure, and *Travertine* when its structure is compact. The latter variety occurs abundantly in Italy, where it is used as a building stone.\* The *stalactites* and *stalagmites*, which are found in limestone caves and arches, originate in a similar way.

Green plants are endowed with the power of *decomposing* carbon dioxide, that is, of separating it into its elementary constituents, carbon and oxygen. The carbon is retained and assimilated by the plants, the oxygen being set free. The process of decomposition is carried on only in the presence of sunlight; during the night this process of assimilation ceases.†

This remarkable power possessed by plants of splitting up carbon-dioxide, absorbing its carbon and setting free its oxygen,

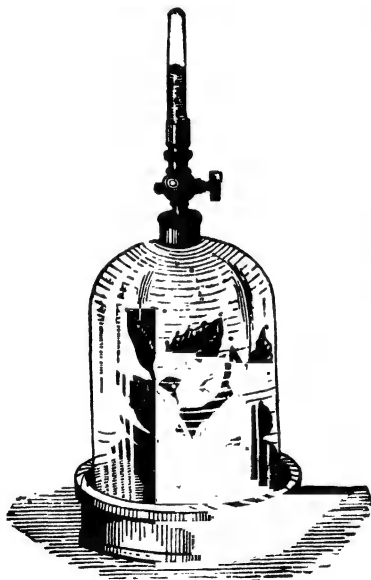


Fig. 42.

\* The celebrated temples of Rome are constructed of Travertine.

† The *respiratory* process by which plants, like animals, take in oxygen and exhale carbon-dioxide goes on at night as well as by day, but in day-light the carbon-dioxide thus given out is at once decomposed and its carbon assimilated, while its oxygen is set free.



may be experimentally illustrated by putting this freshly cut plant( with green leaves) into a tray of water and covering it with a large jar of water saturated with carbonic acid gas, and then exposing the whole apparatus to the light of the sun. As it requires several hours' exposure to the sun to obtain the test-tube half full of oxygen by the process of decomposition, the experiment cannot be completed during our lecture hour. My assistant will now place it in the garden, and if you will come back here after the lapse of a couple of hours, I expect I shall be able to show you that the gas which will then occupy the test-tube will have properties different from those of the gas which now occupies it,\* and, instead of extinguishing a taper, as the gas now there would do, will then cause the taper to burn more brilliantly; it will also lose its property of giving a milky appearance to lime-water; in fact, instead of carbon-dioxide, we shall then have oxygen in the tube.

Under a pressure of  $35\frac{1}{2}$  atmospheres at the temperature  $0^{\circ}$  C., carbon dioxide gas is converted into a clear liquid, similar in appearance to water. When the pressure is removed from the liquid, a large quantity of it suddenly becomes vapour, and the cold produced by the evaporation freezes the remainder into a snow-like crystalline solid, having a temperature of about  $-78^{\circ}$  C. This solid, when dissolved in ether, is used as a freezing mixture for bodies which require a great reduction of temperature to make them solidify. Such a mixture is one of the most powerful means yet discovered for the production of cold (*i.e.* for the abstraction of heat). A temperature as low as  $-110^{\circ}$  C. can be obtained by the volatilization of solid

\* Though the tube is full of water, it is also full of carbonic acid gas, for water dissolves its own volume of this gas.

carbonic-dioxide and ether within the exhausting receiver of an air-pump.\*

### CARBON-MONOXIDE.

Molecule,  $\text{CO} = 28$  ; Density = 14.

Carbon-monoxide (or carbonic oxide) does not occur in Nature ; it is altogether an artificial product.

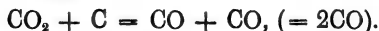
**Preparation.**—This gas is easily prepared from carbon-dioxide, either by removing half its oxygen, or by causing it to combine with an additional quantity of carbon. Thus—



The first process may be illustrated by passing a stream of well dried carbon-dioxide through a red-hot iron tube ; the iron while hot deprives the carbon-dioxide of half its oxygen, and consequently converts it into carbon-monoxide. The decomposition which takes place is shown by the following equation :—



The second process is best illustrated by passing dry carbon-dioxide over red-hot charcoal contained in an iron tube, like a gun-barrel. In this way each molecule of carbon-dioxide parts with half its oxygen, which uniting with an atom of carbon forms a new molecule of carbon-monoxide. Thus—



Carbon monoxide is, however, usually prepared for experimental purposes in the laboratory by heating hydric

\* The lowest temperature yet observed (viz.  $-140^\circ\text{C}.$ ) was obtained by evaporating solidified nitrous oxide dissolved in carbon-bisulphide under the exhausting receiver of an air-pump.

sulphate (sulphuric acid) on crystallized oxalic acid,  $C_2H_2O_4 = (C_2O_3H_2O)$ . The hydric sulphate deprives the oxalic acid of a molecule of water  $H_2O$ , leaving  $C_2O_3$ , which cannot exist in the separate state, and therefore splits up into carbon-dioxide and carbon-monoxide—



By shaking up the mixture with a solution of caustic soda or potash, the carbon-dioxide is removed in the form of carbonate of sodium or carbonate of potassium, and the monoxide alone is left behind.

Here are some jars full of the gas ; it was prepared by the method just described, and collected free from carbon-dioxide by passing the mixed gases through a wash-bottle containing a solution of caustic potash (see Fig. 41).

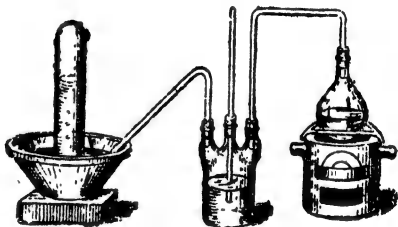


Fig. 41.

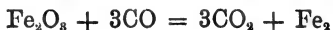
**Properties.**—You perceive that it is colourless, and almost odourless ; it has a poisonous action, like that of carbonic anhydride, on the animal economy—producing death if inhaled. It is even more poisonous than carbonic anhydride. A burning taper is, you see, extinguished when immersed in a jar of this gas ; but, like hydrogen, it burns\* at the surface or where it is in contact with air. The colour of its flame is *light blue*. When mixed with

\* Producing carbon-dioxide.

half its volume of oxygen and ignited, it explodes with a sharp report, producing the dioxide,  $\text{CO}_2$ .

In consequence of its strong affinity for oxygen, it forms a powerful reducing agent, and is employed as such in the large furnaces for reducing iron ore. The air being freely admitted at the bottom, the carbon of the burning coal is converted into carbon-dioxide, which in ascending through the furnace meets with more red-hot coals, some of the carbon of which throws itself into the carbon-dioxide and combines with half its oxygen, thereby reducing it to the state of carbon-monoxide:  $[\text{CO}_2 + \text{C} = 2\text{CO}]$

this gas (CO) then, meeting with the ores (oxides) of iron, takes up oxygen, and reverts to the state of carbon-dioxide



Carbon-monoxide is thus the chief agent in the *deoxidation* of the ore. When the smelter sees a blue flame ascending from the furnace, he knows that some of his *reducing power* is being wasted; and therefore considers the appearance of this blue flame, at the top of the furnace, a sufficient signal to add more ore.

When carbon burns in a limited supply of oxygen, carbon-monoxide is produced, as well as carbon-dioxide; and, in consequence of the more poisonous effects of the monoxide, it is very injurious to health to do what some people are so apt to do in cold seasons—viz. to keep charcoal burning in dwelling-houses in open vessels without chimneys, such as braziers (*segris*) or such like contrivances. Death frequently occurs from ignorantly using charcoal fires without sufficient ventilation. Suicides have sometimes adopted a similar method of cutting short their unhappy lives.

*Familiar Carbonates.*

Sodic carbonate	Barilla, washing soda	$\text{Na}_2\text{CO}_3$
Hydric sodic carbonate	Bicarbonate of soda	$\text{NaHCO}_3$
Potassic carbonate	Potash, pearlash, salt of tartar	$\text{K}_2\text{CO}_3$
Magnesian carbonate	So-called 'magnesia'	$\text{MgCO}_3$
Calcic carbonate	Chalk, marble, limestone, &c.	$\text{CaCO}_3$
Zincic carbonate	Calamine	$\text{ZnCO}_3$
Plumbic carbonate	White lead ore	$\text{PbCO}_3$
Ferrous carbonate	Spathic iron ore	$\text{FeCO}_3$
Cupric carbonate	Malachite	$\text{CuCO}_3$

## CHAPTER XVIII.

### THE ATMOSPHERE.

The atmosphere—from ἀτμός (*atmos*) vapour, and σφαῖρα (*sphaira*) a sphere—or aërial ocean that covers the earth, is neither an element nor chemical compound, but a mechanical mixture of gaseous (or aëriform) bodies; it is, therefore, not represented *symbolically*. From the time of Aristotle till the latter part of last century, *air* was regarded as one of the *four elements* of which, as the ancients fancied, the earth was composed. Its true composition was first determined by Lavoisier.

**Composition.**—You are already aware that the *main constituents* of the air we breathe are *nitrogen* and *oxygen*. The relative proportions of these gases present in the atmosphere have been well determined by Regnault, and the average result of his numerous analyses, conducted with the utmost degree of accuracy, is (per 100 parts)—

	<i>By volume.</i>	<i>By weight.</i>
Nitrogen.....	79·07	76·87
Oxygen .....	20·93	23·13
	<hr/> 100·00	<hr/> 100 00

Or, in *round numbers* more easily remembered—

	<i>By volume*.</i>	<i>By weight.</i>
Nitrogen.....	79	77
Oxygen .....	21	23
	<hr/> 100	<hr/> 100

The existence of small quantities of other gaseous bodies in our atmosphere has been proved by direct experiment.

\* As a means of recollecting, or rather of reproducing these numbers should they be forgotten, the following approximate *rule* will be found useful:—Describe a square, and let it represent 100 volumes of air; inscribe a circle in this square. The circle will represent the proportion of nitrogen, and the corners of the square the proportion of oxygen, by volume (approximately).

The principal of these, and their relative proportions by volume, are as follow :—

Carbonic anhydride .....About 4 parts in 10,000 of air,  
or .04 per cent.

Moisture (aqueous vapour). Variable; usually from 1 to  
1.5 per cent. in Great  
Britain.

Ammonia .....Variable; usually only a trace.

Nitric acid .....Found in the air which falls  
during a thunderstorm.

Ozone .....Usually present in very  
minute quantities.

Hydrogen sulphide .....A trace; the tarnishing of  
silver is an evidence of its  
presence.

Traces of inorganic and }  
organic substances, as } Occasionally present.  
dust, &c. }

Of these, carbonic anhydride, moisture, and ammonia appear to be *essential constituents* of the earth's atmosphere. The following table shows the average composition of atmospheric air, taking account *only* of its *essential constituents* :—

<i>By volume.</i>	
Nitrogen.....	78.00
Oxygen .....	20.70
Moisture .....	1.25
Carbonic anhydride .....	0.04
Ammonia .....	Variable traces.
<hr/>	
99.99	

The constancy of the composition of the atmosphere\* at

\* Notwithstanding the *almost invariable* composition of air, it is not a chemical compound, but a mechanical mixture of the gases above enumerated. The following facts may be mentioned in support of this statement: The *proportions* of its constituents are not *atomic*. Water dissolves air, and air so dissolved contains more oxygen in proportion to nitrogen than undissolved atmospheric air. Its constituents are separable by diffusion. Its density and refrangibility are the *arithmetic means* of those of its component gases.

different times, and in different places, is probably due to a variety of causes, such as heated currents, trade winds, the balancing actions of animal and vegetable life upon it, but more than all to the diffusive power of gases.\*

Such an atmosphere is necessary to the existence of life—animal and vegetable: its constituents (those which I have just enumerated) are of two kinds:—

- (1) Those which are essential to animals;
- (2) Those which are essential to the growth of plants.

The former class consists of oxygen and nitrogen, the latter of carbonic anhydride, ammonia and moisture—though, indeed, a moist atmosphere may be said to be quite as indispensable to the animal, as it is to the vegetable, kingdom.

There are many methods of determining the relative proportions of nitrogen and oxygen present in the atmosphere, the most accurate of these being the method of explosion in the Eudiometer from εὔδιος (*eudios*), good, and μέτρον (*metron*), a measure.†

This apparatus (Fig. 42) is first filled with water, some of which is then spilled out, and a quantity of air allowed into the open leg: the air is made to transfer itself into the sealed leg by skilfully inclining the apparatus. The volume of air contained in the apparatus (when



Fig. 42.

\* If gases did not possess the property of *diffusion*, the several constituents of our atmosphere would arrange themselves in layers in the order of their densities; the carbon-dioxide (being the most dense) would then cover 'the face of the earth,' and make animal existence thereon an impossibility.

† A measure of the goodness of air: its goodness depending on the quantity of oxygen it contains.



the level of the water in both legs is the same) is now read off. Let us call this volume  $V$ , which must not be above 66 per cent. of the volume of the graduated leg. The open leg is then filled with, and inverted over, water. Hydrogen is now passed into the eudiometer, the volume of which should not be less than half that of the air employed. I now close the mouth of the open leg with my thumb, and inclining the instrument, pass all the mixture into the sealed leg. When the water in both legs has the same level, I read the volume of the mixture which we shall call  $V'$ . Again, pouring water into the open tube till it is nearly full, I close it as before, leaving an elastic cushion of air under my thumb, and fire the mixture by means of an electric spark\* from an electrophorus or Leyden jar.

The explosion being over, I again bring the water in both legs to the same level and read off the residual volume,  $V''$ . We know beforehand that when hydrogen and oxygen are exploded in this way they combine to form water, and therefore two volumes of hydrogen and one volume of oxygen *disappear* in the explosion; consequently *one-third* of the loss by the explosion represents the volume of oxygen which has disappeared.

But  $V' - V''$  represents the diminution of volume, therefore  $\frac{V' - V''}{3}$  represent the oxygen contained in ( $V$ ) the volume of air experimented upon.

A tolerably accurate determination of the relative proportions of nitrogen and oxygen in air may be made in the following manner:—

Some air is introduced into a graduated tube standing over water (Fig. 43), and the

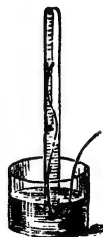


Fig. 43.

\* The spark passes through the platinum wires which are sealed into the upper portion of the closed tube.

volume\* it occupies recorded. A little pellet of phosphorus fixed to an iron wire is then inserted in the tube, and allowed to remain there for some hours—or till all the oxygen is absorbed. The phosphorus is then withdrawn by the wire, and the residual volume (after levelling the water inside and outside) is again read off. The diminution of volume is thus found to be nearly 21 per cent.

As ammonia is a gas, and is always produced during the spontaneous decomposition of azotized† organic matter, it is natural it should be found in the atmosphere.‡ When rain falls it brings the ammonia down with it; and the following are the quantities of it found by different chemists in 1,000,000 grains of rain:—

	Grains.
Rain in Paris during the last five months of 1851 (Barral) ..	3·4900
Rain at Liebfrauenberg in 1852 (Roussingault) .....	0·7440
Rain at Rothamstead in 1853 and 1854 (Lawes and Gilbert)	1·0345

These results indicate,—what might indeed have been anticipated,—that the amount of ammonia in the air is subject to considerable variation, and that it is highest in populous places, where the exhalations of decomposing animal matters are necessarily most abundant—(Apjohn).

The existence of moisture in the atmosphere is easily shown by putting some ice into a glass vessel and allowing it to stand in a warm place for a short time, when the vapour of water will condense like dew on the outer

\* The volume must be read off when the water, inside and outside the tube, stands at the same level.

† That is, containing *azote* or nitrogen.—S.C.

‡ The presence of ammonia in the atmosphere may be detected by drawing a large volume of air (by means of an aspirator) through hydrochloric acid, with which it forms ammoniac chloride, which when treated with caustic lime gives off ammonia gas ( $\text{HN}_3$ ), recognisable by its odour and the white fumes it gives with a rod moistened with HCl.

surface of the glass ; there ! now you can see little drops of water sticking on to this glass ;—and by exposing a known weight of calcium chloride or of dihydric sulphate (both of which possess great power of absorbing water) in a confined portion of air, for a few hours, the weight of the exposed substance will be increased, and thus the quantity of absorbed water can be ascertained.

The presence of carbonic acid gas in the atmosphere may be demonstrated by exposing a solution of lime-water or (better still) baryta-water in an open vessel to the air. The clear solution becomes turbid after a while, in consequence of the carbon-dioxide entering into combination with the lime or baryta, thus forming an insoluble carbonate.

This result can be obtained more quickly by drawing a current of air, by means of an aspirator, through lime or baryta water, when the clear liquid rapidly becomes milky in appearance, owing to the formation of calcium or barium carbonate.

The quantity of carbonic anhydride in any given volume of air is usually found by passing the air (previously dried) through a known weight of a solution of caustic potash ; when all the air has passed through, the increase of weight in the potash solution is the weight of carbonic anhydride present.

**Properties.**—I must now explain to you the *useful properties* of the several constituents of atmospheric air. First, then, we have *nitrogen* and *oxygen*. These, I have said, are essential to animals. That oxygen is essential to animal life can easily be proved by inserting a small animal in a jar of air deprived of its oxygen. Oxygen, then, is the gas whose presence in air gives it the power of supporting animal respiration.\* Animals

\* Recent investigations have shown that oxygen is quite as necessary to the respiration of plants as it is to that of animals.

inhale oxygen, which, meeting with the venous blood in the lungs, combines with and rapidly oxidizes it. This renewed blood is then sent through the body as arterial blood; it is again returned to the lungs, by the veins, charged with an excretion of carbon-dioxide, which is finally exhaled into the atmosphere. This process goes on continually, so that the respiration of animals forms a *constant source* for the supply of carbon-dioxide to the atmosphere.

The use of nitrogen in the atmosphere is not so obvious as that of oxygen. In consequence of its inertness and negative qualities, nitrogen is commonly regarded as a very indifferent body. In a former lecture we learned that nitrogen and oxygen do not readily combine with each other, and that though they may be made to do so at a very high temperature (and actually do combine in small quantities to produce nitric acid during a thunder-storm), yet the heat evolved during their combination is *insufficient* to continue the same: consequently, an atmosphere of nitrogen and oxygen cannot easily be set on fire; it is, therefore, a *safe medium* in which to 'live, and move, and have our being.'

Suppose that, in place of having nitrogen or nitrogen and oxygen, we had pure oxygen as our atmosphere, what would become of us? You know very well that a piece of iron lit in a jar of oxygen goes on burning to the end. When you see a fire in an iron grate, imagine where the grate would go to if the whole of the atmosphere were oxygen. The grate would burn up more powerfully than the coals; for the iron of the grate itself is even more combustible than the coals which we burn in it. A fire put in the middle of a locomotive would be a fire in a magazine of fuel if the atmosphere were oxygen.—(Faraday.)

As animal life and heat are maintained by a kind of slow combustion, which we call *eremacausis*—*i.e.* combustion without flame—it is plain that if animals be compelled to breathe pure oxygen, the chemical action to which life is due would become so rapid as to throw them into a state of feverish excitement, which would, no doubt, prove fatal. Life would thus become shorter than it is in our present atmosphere. We may therefore conclude that the object of nitrogen is to *dilute* the oxygen, so as to prevent too rapid a consumption of life and fuel.\*

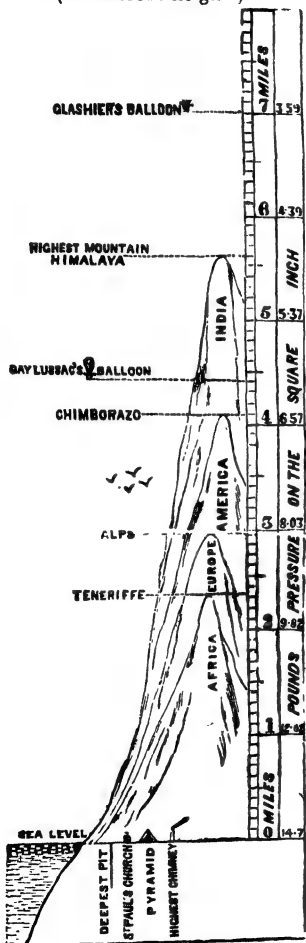
The compensating actions of the animal and vegetable kingdoms on each other, and the duties performed in the latter by the moisture, carbonic anhydride and ammonia of the atmosphere, are thus described by a modern writer of high reputation† :—

‘The natural food of plants consists chiefly of *water*, *carbonic acid* and *ammonia*, together with small quantities of mineral salts varying with the kind of plant. The natural excretions of the animal kingdom consist of *water*, *carbonic acid* and *urea*, which is rapidly converted into *carbonate of ammonia*, together with some mineral salts, in general similar to those used in the food of plants, such as phosphates and other salts of magnesia, soda, potash, &c. These two kingdoms of Nature thus compensate each other’s action, the excretions of one forming the food of the other, and *vice versa*. The carbonic acid excreted by the lungs of animals and produced by the combustion of coal and wood becomes a constituent part

\* ‘Nitrogen, however, also serves an important purpose in the economy of nature, by increasing the volume of the atmosphere without conferring upon it *active chemical properties*. Provision is thus made for the occurrence of winds, the tempering of climate, the diffusion of heat, the scattering of the sun’s light, and the realization of other useful ends *essential* to the welfare of man and the other living inhabitants of the globe.’

† Professor Haughton, of Dublin.

Pressure of the atmosphere  
(at different heights).



of the air we breathe, and would destroy animal life if it attained to four per cent. of that air: but by the wonderful compensation of the vegetable kingdom it is absorbed by the leaves of plants in respiration,\* and resolved into carbon and oxygen; the former of which becomes fixed in the woody fibres of the plant, while the oxygen is given back to the atmosphere, and renders it again fit for the respiration of animals. The *urea* excreted by the kidneys of animals is rapidly converted into carbonic acid and ammonia, both of which are dissolved by moisture and conveyed to the roots of plants, whence they are pumped up by *endosmotic* force into the leaves.'

Pure air is colourless, tasteless, odourless; it is 14.47 times as heavy as hydrogen,—the *weight* of 1 liter at standards being 1.293187 gram.

The presence of *dust* in

\* *Assimilation* would probably be a more correct term.—S. C.

the air, reaching up to considerable heights, by its effect in polarizing sunlight, produces the blue colour of the sky, which we so frequently admire. Above the atmosphere the sky appears pitchy black. The atmosphere exerts an average pressure (at sea level) of 1·0333 kilogram per square centimeter of area—or 10·333 kilograms per square meter, which is the weight of a column of mercury 760 m.m. high, standing on a square base, each side of which is one meter in length. In the diagram on the previous page the column to the right gives the pressure of the atmosphere in pounds on the square inch at various well-known heights—starting with 14·7 lbs. on the square inch at sea level.\*

The atmosphere is *supposed* to extend to a height of about 45 miles: this supposition, however, is based on *facts* connected with the phenomenon of twilight. That is, the light which illuminates the atmosphere for some time both after sunset and before sunrise. It results from the reflection and refraction which the rays of light undergo in passing through the various strata of air, owing to which the light of the sun is *dispersed* by the atmosphere till he descends about 15° or 18° below the horizon.

\* As the height above sea level increases in arithmetic ratio, the density of the air decreases in geometric ratio.

## CHAPTER XIX.

### COMBUSTION (FIRE AND LIGHT).

Combustion in the general sense is but a relative term, and, as previously noticed, may be applied to any chemical action whatsoever when accompanied with the evolution of heat. *Ordinary combustion*—or the *fire* which results from the burning of such combustible materials as coals, oils, candles, coal-gas, &c., in atmospheric air—is due to a violent chemical combination of the free oxygen of the air with the elements of the combustibles, or inflammable materials, by which both heat and light are evolved, and the chemical action thus produced is termed *oxidation*. Bodies which undergo combustion, *i.e.* burn in air, burn more brilliantly in pure oxygen, as we have already seen when examining the properties of that gas.

It is commonly supposed that when any substance is burned, the matter of which it was composed is lost, or becomes annihilated. That this is a *popular fallacy* is easily proved by direct experiment ; the following simple experiments will, I hope, satisfy you :—Having carefully weighed a porcelain crucible containing a little metallic wire, I burn the wire by placing the crucible over a hot flame :—when burnt and allowed to cool, we shall find the crucible and its contents heavier than before the wire was burnt. Here then we see that there is *no loss*, but on the contrary an actual increase of matter by burning the metal (magnesium), the increase being the weight of the oxygen which left the atmosphere to combine with the metal while burning, *i.e.* oxidising. A similar experiment may be made by burning phosphorus



in air and weighing the produce of combustion. Or we may burn a candle in a tube and collect and weigh the carbonic acid and waters produced by its combustion.\* In all cases the products of combustion (though generally gaseous and invisible) will be found to be heavier than the original materials burnt.

The definite *initial temperature* (differing for different substances) necessary to start the combustion of a combustible body is termed its *igniting point*. As the intensity of the heat evolved by the same combustible materials depends on the rapidity of combination, so the rapidity of combination depends on the rate at which oxygen, and therefore air, is supplied. The only difference between combustion and *explosion* is rapidity of combination. The effect of chimneys is, by creating a draught, to increase the quantity of air supplied in a given time, and thus increase the rapidity of combination, and therefore the intensity of the heat obtainable.

From experiments conducted on the top of Mont Blanc by themselves, Dr. Frankland and Professor Tyndall have determined the influence of height on combustion. They found that the illuminating power of a candle flame was greatly diminished,† but that strange to say, the quantity of material consumed in a given time was the same on the top of the mountain as in the valley below.

Ordinary combustible materials, those which are used for heating and illuminating purposes (coals, wood, oils, candles, coal-gas, &c.) are chiefly composed of carbon and hydrogen, and their compounds termed *hydrocarbons*, as Marsh gas ( $\text{CH}_4$ ), Olefiant gas ( $\text{C}_2\text{H}_4$ ), and Oil gas, &c., &c.

\* By passing the gaseous products through a caustic potash tube attached to the tube containing the candle, the water and carbonic acid remain in this tube.

† The difference of illuminating power evidently depended on difference of pressure.

The fire which accompanies combustion is either incandescence or flame; it is termed incandescence (or *glow*) when the burning body is not converted into the gaseous state before combustion actually takes place\*; it is called flame when the body attains the gaseous condition before rapid combustion ensues. Flame, then, in the ordinary acceptation of the term, is a column of highly heated gas undergoing combustion by combining with the oxygen of the air.

All flames are not equally luminous, and the principle upon which all practical methods of illumination depend is, that a *heat-producing material* and an *incandescent solid* should exist in the substances employed for illumination, and that the burning of the former should set free the latter, yielding at the same time, by combustion, the necessary temperature to render it luminous. Thus with *coal gas*, which is a mechanical mixture of several gases, chiefly hydro-carbons,† the hydrogen of the hydro-carbons, as in the case of Olefiant gas, *first* enters into union with the oxygen in the air, and by its combustion yields heat sufficient to make the carbon, which in a fine state of division pervades the flame for a time, *glow*; it is to the presence of this *incandescent carbon* that the great illuminating power of the flame is due. The carbon finally combines with oxygen and passes away as carbon-dioxide. More *solid* carbon is separated from its combination with hydrogen, as more gas is burned, thus keeping up a continuous light-giving flame.‡ I shall now

\* Some bodies, such as platinum, lime, &c., became incandescent, without burning, when intensely heated; a platinum wire or a piece of lime may be made *white hot* without undergoing any chemical change.

† Consisting of Marsh gas  $\text{CH}_4$ , Olefiant gas  $\text{C}_2\text{H}_4$ , and other hydro-carbons of the general formula  $\text{C}_n\text{H}_{2n}$ .

‡ Prof. Frankland has recently shown that a luminous flame may be obtained, *without incandescent solid particles*, by burning gases under increased pressure.

prove these statements by experiments on Marsh and Olefiant gases, samples of which are being prepared before you on the table. They are the two most important compound gases contained in the complex mixture known as coal-gas. Marsh gas is prepared by heating together sodium acetate and sodium hydrate in a copper retort— $\text{NaC}_2\text{H}_3\text{O}_2 + \text{NaHO} = \text{CH}_4 + \text{Na}_2\text{CO}_3$ . Olefiant gas is obtained by heating alcohol with oil of vitriol in a flask fitted with a delivery tube— $\text{C}_2\text{H}_5\text{O} + \text{H}_2\text{SO}_4 = \text{C}_2\text{H}_4 + \text{H}_2\text{O}, \text{H}_2\text{SO}_4$ . A good mixture for preparing Olefiant gas is 1 vol. of alcohol and 4 vols. strong oil of vitriol mixed with sand to prevent frothing up.

Both these gases extinguish the taper, but like hydrogen burn at the surface of contact with air; and when mixed with oxygen form explosive mixtures. Olefiant gas is an illuminating body, for it deposits carbon on being strongly heated (as when it is burning), evidenced by its depositing soot on any cold body which is introduced into the flame.

The light evolved during combustion having been satisfactorily accounted for, it remains to notice some of the recent theories which have been put forward to account for the heat of combustion, on which the light evidently depends,—as bodies raised to a high temperature always emit light.

Two chemists, named Craufurd and Irvine, suggested that the heat evolved during combustion might be accounted for by the doctrine of specific heats. They maintained that the heat evolved during the formation of a compound by combustion was due to the specific heat of the compound being less than the mean of the specific heats of its components. This theory does not take into account

the heat absorbed or evolved when a body undergoes a change of state, and is consequently considered defective.

Another very ingenious theory, first announced by Berzelius and Davy, and afterwards supported by the celebrated Frenchman Ampère, is thus concisely explained by Professor Apjohn :—‘The atoms of all bodies have peculiar electric states, which they never lose, some being negative and some positive. Each atom, however, is encompassed by an atmosphere of electric fluid of an opposite nature to its own, and which is produced around it upon the principle of induction. Dissimilar atoms combine chemically in virtue of being in opposite electric states, and the light and heat attendant upon their combination are, like those of the common electric spark, due to the union of the electricities of the electric atmospheres which combine with and neutralize each other.

Professor Tyndall, in extending Waterston’s meteoric theory of solar heat from the Sun and Planets to *chemical atoms*, appears to ascribe the heat of combustion to the *clashing together of atoms*, by which their motion is converted into heat—as the following quotation from his celebrated work ‘Heat a Mode of Motion’ will show :—

‘A diamond is pure carbon, and carbon burns in oxygen. Here is a diamond, held fast in a loop of platinum wire; heating the gem to redness in this flame, I plunge it into this jar, which contains oxygen gas. See how it brightens on entering the jar of oxygen, and now it glows like a little star with a pure white light. How are we to figure the action here going on? Exactly as you would present to your mind the idea of meteorites showering down upon the sun. The conceptions are, in

quality, the same, and to the intellect the one is not more difficult than the other.

You are to figure the atoms of oxygen showering against this diamond on all sides.

They are urged towards it by what is called chemical affinity ; but this force made clear presents itself to the mind as pure attraction, of the same mechanical quality, if I may use the term, as gravity. Every oxygen atom as it strikes the surface, and has its motion of translation destroyed by its collision

with the carbon, assumes the motion which we call heat ; and this heat is so intense, the attractions exerted at these molecular distances are so mighty, that the crystal is kept white-hot, and the compound, formed by the union of its atoms with those of the oxygen, flies away as carbonic acid gas.'

The flame\* of a common candle was long a problem for the study of chemists, till Davy by dissecting it revealed its true structure. The flame of a candle is essentially the same in nature as that of a jet of coal-gas, and may be divided into *three distinct conical spaces*. First, there is a visibly dark conical core of unburnt gas. This is technically called the *area of no combustion*, and is represented by the space marked *a* in Fig. 45. Secondly, there is a luminous cone immediately surrounding the dark, or non-luminous one. This luminous cone



Fig. 44.

\* In its widest sense by flame we denote a column of highly-heated gas undergoing combustion, by chemically combining with some other gas.

deposits soot when its temperature is reduced by the introduction of a cold body into it. This second cone is therefore termed the *area of partial combustion*; it is represented by the white space marked *b* in the figure. Thirdly, there is an outer cone, scarcely visible but much hotter than the inner luminous one; this third cone is termed the *area of complete combustion*, since in it the carbon is completely burnt, producing the gaseous compound carbon dioxide which flies away as fast as formed. This cone is represented by the space marked *c* in the accompanying figure.

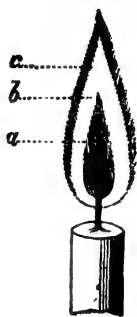


Fig. 45.

When a current of air is forced into the flame of a candle by means of a mouth *blowpipe* (see Fig. 46), the 'area of no combustion' cannot exist,\* while the 'area of complete combustion' becomes mingled with an excess of oxygen. The ordinary flame is thus converted into two zones: an *inner* one—which, owing to the presence of incompletely oxidized hydrocarbons, has a powerful *reducing* action on metallic oxides—termed the *reducing flame*; and an *outer* one, technically called the *oxidizing flame*, as in consequence of the excess of oxygen supplied, in conjunction with the high temperature resulting from complete combustion, it possesses great power of *oxidizing* bodies brought into its zone. Thus a small piece of lead

\* As the oxygen contained in the current of air causes a *partial combustion* of the hydrocarbons which, under ordinary circumstances, form the conical core of *unburnt gas*.

is rapidly oxidized when held in the tip of the outer flame, while the oxide thus formed is again reduced to the metallic state when supported, on charcoal, in the inner (or reducing) flame for a few seconds.



Fig. 46.

The blowpipe is an instrument much used by practical chemists in testing the nature and qualities of mineral substances.\*

#### DISTILLATION OF COAL AND WOOD.

When coal is subjected to dry distillation in iron or clay retorts from which air is excluded, the coal becomes resolved into a great variety of new bodies ; this process is known by the term *destructive distillation*, though the coal is not actually annihilated, but new products are formed by the re-arrangement of its atoms.

\* The blow-pipe characters of the common metals will be found in the Author's Test Tables for Analysis.

The new products formed may be arranged in four classes :—

1. **Coal-Gas** :—Consisting of a variety of gaseous compounds.

2. **Coal-Tar** :—A strong smelling oily black liquid.

3. **Ammonial Liquor, or Gas-water** :—Containing salts of ammonia.

4. **Coke** :—The residue left in the retorts.

The full description of the methods of preparing coal-gas belongs to a work on Technical Chemistry. I will not attempt more here than to give a brief summary of its composition and properties.

The crude gas may be said to consist of a mechanical mixture of the following gaseous bodies :—

<i>Name.</i>	<i>Molecular formula.</i>	<i>Approximate percentage.</i>
Hydrogen .....	H <sub>2</sub>	..... 45·5
Marsh gas .....	CH <sub>4</sub>	..... 34·9
Olefiant gas.....	C <sub>2</sub> H <sub>4</sub>	..... 4·1
Oil gas .....	C <sub>4</sub> H <sub>8</sub>	..... 2·4
Carbon monoxide .....	CO	..... 6·6
Carbon dioxide .....	CO <sub>2</sub>	..... 3·7
Hydrogen sulphide .....	H <sub>2</sub> S	..... 0·3
Nitrogen .....	N <sub>2</sub>	..... 2·4
Ammonia .....	H <sub>3</sub> N	..... variable.
Cyanogen .....	(CN) <sub>2</sub>	..... trace.
Benzole vapour .....	C <sub>6</sub> H <sub>6</sub>	..... „
Naphthalene vapour .....	C <sub>10</sub> H <sub>8</sub>	..... „
Carbon disulphide vapour	CS <sub>2</sub>	..... „
Water vapour.....	HO	..... variable.

Many of these gases do not burn, and would, therefore, be better removed, while others, such as carbon disulphide and hydrogen sulphide, are very offensive in odour, and



would also yield irrespirable products by combustion. Hence the necessity for a complicated process of purification of crude coal-gas, before being employed for the illumination of our houses and the heating of our stoves, &c.

Purified coal-gas will usually contain hydrogen, marsh gas, olefiant gas, oil gas and other vaporous hydro-carbons, also carbon monoxide and nitrogen; the relative proportions in this mixture depending principally on the quality of coal used in the manufacture. From what we have already studied in reference to combustion it appears that the value of coal-gas, as a source of light, must depend on the nature and amount of its *hydro-carbon* constituents. By means of a Bunsen's burner, with which I shall now proceed to experiment, I will show you how I may, at will, produce either a luminous or a heat-giving flame. The lighted taper is extinguished when immersed in a vessel filled with coal-gas, but like hydrogen the gas burns at the surface or where it is in contact with air. When mixed largely with air it assumes a violently explosive character; hence another danger arises in leaving gas jets open at night in bed chambers, in addition to its irrespirable and poisonous properties when inhaled in large quantity.

**Wood-Gas:**—In many towns on the continent of Europe, gas obtained from the destructive distillation of wood is used as a substitute for coal-gas; but its illuminating power, owing to its containing less of the heavier hydro-carbons, is much inferior to that of average coal-gas. By comparing the relative composition of wood and coal we find that the former contains a much larger proportion of oxygen than the latter, and hence the products obtained from its destructive distillation are naturally more highly oxidized (or so to speak already

partially burned). They consist of a mixture of the oxides of carbon, water, hydrogen, and marsh gas, also acetic (pyroligneous) acid, wood naphtha (wood spirit) and wood-tar, &c., &c. On this subject we cannot go further without trespassing on the bounds of Organic Chemistry.

Approximate Analysis of Wood and Coal.

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Wood (dried oak) . . .	51.5	5.8	42.4	0.2
Coal (Bituminous) ..	79.5	5.5	13.0	1.9

Though I can now give you credit for a better knowledge of the four *ancient* elements—**earth, water, air, fire**—than the Ancients themselves possessed, yet I am bound to warn you of the possibility of a return, in the near future, to the theory of the more ancient philosophers, who held that there exists but one variety of material—the *essentia*, or essence of matter. Already we have arrived at the 'Periodic Law' of Mendelejeff,\* which maintains that the properties of an element are functions of its atomic weight. And if, in addition, we admit the truth of Prout's hypothesis (known as Prout's law), that the atomic weights are all *multiples by whole numbers* of that of Hydrogen, we see how near we approach the idea of the unity of matter.

\* A tabular statement, illustrative of the Periodic Law, will be found overleaf. It is also known as Newlands' and Mendelejeff's law. Newlands was the first to suggest that, when arranged in the order of their atomic weights, the elements show a *periodic recurrence of similar properties*. Thus a natural classification of the elements into groups, similar to the smaller groups already noticed, is possible.

The 'Periodic Law' supposes a *periodic variation* in the chemical properties of the Elements in correspondence with increase of atomic weight. Eight groups arranged in 12 series are suggested.

Series.	Group I. ( $R_2O$ )	Group II. ( $RO$ )	Group III. ( $R_2O_3$ )	Group IV. ( $RO_2$ )	Group V. ( $R_2O_5$ )	Group VI. ( $RO_3$ )	Group VII. ( $R_2O_7$ )	Group VIII. ( $RO_4$ )
1	H=1							
2	Li=7	Be=9.2	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.5	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	Ga=69.8	—=72	As=75	Se=79	Br=80	
6	Rb=85	Sr=87	Yt=89.6	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	La=139	Ce=141	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	—	—	Ta=182	W=184	—	Os=195, Ir=197, Pt=197, Au=197
11	(Au=197)	Hg=200	Tl=204	Pb=207	Bi=210	—	—	—
12	—	—	—	Th=231	—	U=240	—	—

## CHAPTER XX.

### CHEMICAL GYMNASIUM.

1. The average height of the standard barometer at sea-level in the latitude of Paris is 760 m.m. Reduce this to its equivalent in inches. Answer, 29.922 inches.

2. The average pressure of the atmosphere is estimated at 10.333 kilograms per square meter of surface. Find the corresponding pressure in kilograms per square centimeter. Answer, 1.0333 kilograms.

3. How many millimeters are equivalent to 33 inches? Answer, 762.

4. Name the measures of length which are longer than the meter, and convert them into their English equivalents.

5. Convert 33,000 foot-pounds per minute into kilogrammeters per second. Answer, 76 nearly.

6. Write out the tables of the *Metric System* in as small a space as you can, consistent with perspicuity and exactness; and briefly contrast its advantages as compared with the old English system of weights and measures.

7. How many cubic feet are there in 105 cubic meters? Answer, 3708.3.

8. The length of Mont Cenis tunnel is about 12.2 kilometers. Find its length in English miles. Answer, 7.58.

9. How would you find the number of centimeters in the edge of a cube whose volume is a hectoliter?

Answer, 4

10. Convert  $25^{\circ}$  Centigrade into its equivalent in Fahrenheit degrees. Answer,  $77^{\circ}$  F.

11. Convert  $30.2^{\circ}$  Fahrenheit into its equivalent on the Centigrade scale. Answer,  $-1^{\circ}$  C.

12. Convert  $-15^{\circ}$  C. into its equivalent in Fahrenheit degrees. Answer,  $+5^{\circ}$  Fahrenheit.

13. The volume of 16 *grams* of oxygen at  $0^{\circ}$  C. and 760 m.m. pressure is 11.2 *liters*. Calculate the volume of 16 *grains* of oxygen (under the same conditions of temperature and pressure), in *cubic inches*. Answer, 44.3 nearly.

14. The old English unit of heat being the amount of heat necessary to raise the temperature of one pound of water through  $1^{\circ}$  Fahrenheit, find the ratio of this unit to the French unit of heat,—or one degree of heat, as defined in Chapter II. Answer, 50 : 198, or 1 : 4 nearly.

15. Find the ratio of a foot-pound (or English unit of work) to a kilogrammeter (or French unit of work). Answer, 1 :  $7\frac{1}{4}$  nearly.

16. What are the three physical *states* in one or other of which all varieties of matter exist? Describe the *viscous* condition.

17. Distinguish between molecular attraction and chemical affinity; in what respects do they agree, and how do they differ?

18. Give concise definitions of (a) *one degree of heat*, (b) *specific heat*, (c) *latent heat*. Of all known substances which has the greatest capacity for heat?

19. Distinguish between a *degree of temperature* and a *degree of heat*—giving illustrations.

20. It is a general maxim in chemical science that extension and rarefaction occasion cold, but that conden-

sation and compression produce heat. Illustrate this by examples.

21. How many degrees of heat are evolved by the fall of 50 kilograms from a height of 1,000 meters?

22. What volume would a cubic foot of air (air being supposed incondensable) occupy at the temperature  $-273^{\circ}\text{C}$ .?

23. Define the following terms in accordance with the modern system of Chemistry:—atomic weight, atomic volume, molecular weight, molecular volume, vapour-density, one gas-volume, specific volume.

24. Distinguish between the *chemical* and *physical* specific gravities of bodies. The chemical *sp. gr.* of steam is 9: determine its physical *sp. gr.*

25. Explain the meaning of the following symbols:  $\text{H}$ ,  $\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{H}_3\text{N}$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $2(\text{H}_2\text{SO}_4)$ .

26. Calculate the vapour-densities of the following bodies:—ice, hydrogen-chloride, ammonia, carbon-dioxide.

27. State (a) the laws of combination, (b) the law of gaseous volume, (c) the law of gaseous diffusion.

28. Describe the changes which the tension of a gas undergoes—

(a) if subjected to a constant pressure,

(b) if contained in a constant volume,

while its temperature is being raised from  $0^{\circ}\text{C}$ . to  $273^{\circ}\text{C}$ .

29. Explain the meaning of the terms *electro-positive* and *electro-negative* when applied to the Elements.

30. When two bodies do not combine on being placed in contact, does that circumstance prove that they have no affinity for each other. Give a reason for your answer.

31. Give a brief description of Dalton's *atomic theory*.

32. Define the term *crith*; and determine its weight both in grams and grains.

33. Calculate the weight of 25 liters of carbonic anhydride at the standard temperature and pressure.

34. What volume would 25 grams of hydrogen occupy at 15° C. and 725 m.m. pressure?

35. If the weight of the air contained in an *air thermometer* be .4645 of a gram, prove that  $VP = \text{absolute temperature}$ .

36. Calculate the weight of a hectoliter of dry air at 15° C. and 720 m.m. mercurial pressure.

37. Explain the meaning of the equation—

$$W = \frac{.0321 V_p}{273 + t} \left( \frac{\text{combining weight}}{n} \right)$$

and show how to deduce it from first principles.

38.—Explain what is meant by the *replacing power* of bodies. What is understood by the *chemical equivalent* of a body?

39. Distinguish between a *salt* and a *compound radicle*.

40. Write a short note on the doctrine of chemical *types*.

41. Explain the distinction between a *rational* and an *empirical* formula, giving illustrations.

42. How may the empirical formula be obtained from the percentage composition?

43. Deduce the empirical formula of a substance which, on analysis, yielded the following percentage composition :—

Potassium.....	28.73
Hydrogen .....	0.73
Sulphur .....	23.52
Oxygen .....	47.02

44. Find the percentage composition of the substance which is represented by the formula  $\text{Ca}_3(\text{PO}_4)_2$ .

45. How is the rational formula of a substance determined?

46. If a cubical box, holding 11.2 liters, be filled with hydrogen, oxygen, nitrogen, and chlorine, successively, at standards: how many grams of each gas would the box contain?

47. How many gas volumes are represented by the symbols  $\text{H}_2$ ,  $\text{O}_2$ ,  $2\text{Cl}_2$ , respectively?

48. What is meant by the term 'standard pressure'? What by 'one atmosphere'?

49. Explain the terms—*acid*, *alkaline* and *neutral* reaction. What are the three alkalis?

50. Explain the use of the terms *mono-*, *di-*, and *tri-basic*, as applied to certain acids.

51. What are the natural sources of hydrogen?

52. From whence is the name *hydrogen* derived?

53. Describe (at least) three different processes for preparing hydrogen, and represent the decomposition in each case by symbols.

54. What quantities of zinc and hydrogen sulphate must be employed to obtain 15 milligrams of hydrogen?

55. What volume would 27 grams of hydrogen occupy at the normal temperature and pressure?

56. What weight of hydrogen-gas (at  $0^\circ \text{C}$ . and 760 m.m.) is required to fill a balloon of 22 hectoliters capacity?

57. What would be the *ascensional force* of the balloon (in last question) supposing it to weigh 1 kilogram when empty?

58. In what sense is Zn *equivalent* to  $\text{H}_2$ ?



59. What are the principal characteristic properties of hydrogen?

60. Describe some experiments which serve to illustrate the inflammability of hydrogen in air.

61. What is formed when hydrogen burns in air?

62. Describe some experiments in illustration of the extreme levity of hydrogen gas. How does an atmosphere of hydrogen affect sounds?

63. What are the natural sources of oxygen?

64. What is the origin of the name *oxygen*?

65. How, and by whom, was oxygen *first* prepared?

66. From what materials is oxygen now generally prepared?

67. Represent, in symbols, the decomposition which potassium chlorate undergoes under the influence of heat.

68. What volume of oxygen gas (at standard temperature and pressure) can be obtained from one kilogram of potassic chlorate?

69. How much chlorate of potassium must be employed to prepare one hectoliter of oxygen, at the normal temperature and pressure?

70. What weight of oxygen (at 0° C. and 760 m.m.) is required to fill a gasometer of 300 hectoliters capacity?

71. A bottle is filled with oxygen gas (at standard temperature and pressure), and then hermetically sealed. At what temperature would the elastic force of the oxygen be sufficient to burst the bottle, on the supposition that the bottle would burst if subjected to a pressure of 2.0666 kilograms per square centimeter?

72. Describe in words, and represent in symbols, the effect of a red heat on pyrolusite.

73. What weight of pure manganese is needed to prepare one liter of oxygen, at the normal temperature and pressure?

74. Describe the principal characteristic properties of oxygen, especially in regard to combustion and respiration.

75. What is ozone? What are its chief characteristic properties? Why are the properties of ozone especially interesting to chemists?

76. In what proportion does water dissolve oxygen gas?

77. How would you show that hydrogen possesses a powerful affinity for oxygen?

78. How is it that a jet of pure hydrogen may be burned in the air, with perfect safety, whereas a mixture of hydrogen and air produces a dangerous explosion if ignited?

79. Explain the meaning of the term *reducing agent* as employed in chemical writings.

80. Describe an experiment illustrative of the *reducing action* of hydrogen.

81. How many grams of *reduced copper* can be obtained by the aid of 2 grams of hydrogen?

82. Describe the construction of Dobereiner's lamp, and explain its action.

83. Explain the principle of the *lime-light*. For what purpose is it now usually employed?

84. With the aid of Priestley's Philosophical Candle, a brass jet and a bladder full of oxygen, how would you produce the *oxy-hydrogen flame*?

85. How may *pure water* be prepared from sea-water? What is the process called? What becomes of the solutions of carbonates thrown into the sea by rivers?

86. Of what elements is water composed?

87. In what proportions (by volume) are the elements of water united ?

88. How did Cavendish determine the composition of water ?

89. How may the original conclusion of Cavendish (with respect to the composition of water) be confirmed (a) by the method of *analysis*, (b) by the method of *synthesis* ?

90. From the known composition of water *by volume* deduce its composition *by weight*.

91. Write down the molecular formula of water, and show that it indicates its composition, both by weight and by volume.

92. How did Dumas determine the percentage composition of water ? Give the average of his results.

93. How much copper will be reduced in the formation of 18 grams of water, and what volume of dry hydrogen (measured at standards) is necessary to reduce it ?

94. How many units of heat are developed by the complete combustion of one kilogram of hydrogen in oxygen ? Supposing the process of combustion to occupy a *second of time*, to how many *Horse Power* is the work produced equivalent ?

95. How does *water* afford a most striking illustration of the fact that compound bodies possess properties different from those of their components ?

96. Describe the principal physical properties of water.

97. What are *hydrates* ? Illustrate your answer by an example. Give an example of an *aqueate*.

98. Explain what is meant by—(a) *water of crystallization*, (b) *constituent water*. Give examples in illustration.

99. Describe, carefully, the effects produced on water—(a) by gradually raising its temperature from  $0^{\circ}\text{C}$ . to  $4^{\circ}\text{C}$ . (b) by gradually lowering its temperature from  $4^{\circ}\text{C}$ . to  $0^{\circ}\text{C}$ .

100. What is the temperature on the Fahr. scale corresponding to the maximum density of water?

101. Explain how it is that fishes can live in the waters of those seas which are constantly frozen over for several months of the year.

102. Explain what is meant by a *saturated solution*.

103. A block of Wenham Lake ice weighs 50.8 kilograms: what is its volume?

104. When a liquid solidifies it evolves heat: how may this statement be verified experimentally?

105. Can water exist in the *liquid state* at a lower temperature than that of *melting ice*?

106. What happens when water at the temperature  $100^{\circ}\text{C}$ . is placed on a fire?

107. Under what general conditions does water enter into *ebullition*?

108. Explain how water may be made to boil by the abstraction of heat.

109. What is the latent heat of water?

110. Define the *boiling point* of water.

111. What is *evaporation*?

112. Why is water called a *neutral oxide*?

113. What are the natural sources of nitrogen?

114. Describe two essentially different methods of separating nitrogen from atmospheric air.

115. How may it be proved that nitrogen is an essential ingredient of animal tissue?

116. Represent, in symbols, the decomposition which ammonium nitrite undergoes on being strongly heated.

117. Describe briefly the principal characters by which nitrogen gas may be recognised. How may it be distinguished from carbonic anhydride? Describe the oxides of nitrogen. How is nitric acid related to them?

118. Mention the names of the natural varieties of carbon, and state the uses of each variety.

119. How may it be proved that the diamond consists of pure carbon?

120. How should a diamond be cut—(a) so as to form a *rose*, (b) so as to form a *brilliant*?

121. How would you estimate the value of a diamond under 20 carats weight?

122. In what kind of rocks, and in what parts of the world, are diamonds usually found?

123. Where was the celebrated 'Kohinoor' found?

124. Describe the appearance and properties of *anthracite*.

125. Mention the names of, and describe the modes of preparing, the principal artificial varieties of carbon.

126. For what purpose is animal charcoal used by sugar-refiners? How is it made?

127. What is ivory-black?

128. What is lamp-black? What is soot?

129. Of what materials is *printing ink* composed?

130. Describe the properties of charcoal, especially those which make it a valuable material for water filters.

131. Account for the occasional *spontaneous combustion* of heaps of charcoal.

132. How many 'degrees of heat' are evolved by the *complete* combustion of 12 grams of pure carbon in oxygen?

133. What volume of air (measured at standards) is necessary for the *complete* combustion of 1 kilogram of pure carbon ?

134. What are the natural sources of carbon-dioxide ?

135. What materials are usually employed (in the laboratory) for preparing carbon-dioxide ?

136. Represent by means of an equation the action of hydrogen chloride on white marble.

137. When 'carbonic acid gas' is required for aërating soda water, what materials are used in its preparation ?

138. Describe the chief characteristic properties of carbon-dioxide.

139. What evidence is there for considering carbon-dioxide to belong to the class of *anhydrides* ?

140. Carbonic anhydride is said to be an extinguisher of combustion ; is this statement *absolutely* true ? Give reasons for your answer.

141. How would you prove that *expired air* contains carbonic acid gas ?

142. Describe fully the effects of a stream of carbonic anhydride on lime-water.

143. What is *Travertine* ? and how is it formed ?

144. What are *Stalactites* and *Stalagmites* ? Describe the process of their formation.

145. How is carbonic acid gas affected by green plants under the influence of sunshine ?

146. How is solid carbonic anhydride prepared, and for what purpose is it used ?

147. Carbon-monoxide may be prepared from carbon-dioxide by one or other of two processes ; describe them, using symbols in illustration.

148. Describe in words, and represent in symbols, the decompositions which crystallized oxalic acid undergoes when heated in contact with hydric sulphate.

149. Describe the chief properties of carbon-monoxide.

150. Describe the chemical changes which take place in the large furnaces for reducing iron ore. Why does the smelter consider the appearance of a *blue flame* at the top of the furnace a sufficient signal to add more ore?

151. Has carbon-monoxide any influence on animal respiration?

152. What are the *main constituents* of the atmosphere? State the proportions in which they are present, by weight and by volume.

153. What other bodies (besides nitrogen and oxygen) are found in the atmosphere?

154. Name the *essential* ingredients of the earth's atmosphere; and state the proportions (by volume) in which they occur.

155. What evidence have we for considering air to be a mechanical mixture rather than a chemical compound?

156. Describe the apparatus known as the voltaic eudiometer.

157. How would you effect the eudiometric analysis of air?

158. With the aid of a pellet of phosphorus, a piece of wire, a graduated tube, and a basin containing water, how would you make a volumetric analysis of air?

159. What is the probable origin of the ammonia which is found in the atmosphere? How would you detect it?

160. How would you detect the presence of aqueous vapour in the atmosphere?

161. How would you demonstrate the presence of carbonic anhydride in atmospheric air ?

162. Mention the principal *useful purposes* served by the several constituents of our atmosphere.

163. Describe briefly the compensative actions of the animal and vegetable kingdoms on the atmosphere ; and hence deduce an argument in support of the *plausible theory* as to the existence of a greater amount of carbon-dioxide in the atmosphere of the carboniferous period (Age of Plants) than exists in that of the present period (Age of Man).

164. When the earth's atmosphere contained 4 per cent. of carbonic acid gas, the higher forms of animals could not have lived in it. If this gas became fixed by combining with lime, calculate the weight of the resulting bed of limestone if spread uniformly over the whole earth.

165. Write a short note on the nature of *combustion*.

166. What weight of ice would be melted by the heat evolved during the complete combustion of *one gram* of hydrogen in atmospheric air ?

167. Explain the general principle involved in the production of luminous flames.

168. What are the chief constituents of coal-gas ? To which of them is the illuminating power of its flame more especially due ?

169. Why does olefiant gas yield a brighter flame than hydrogen ?

170. By the aid of the doctrine of specific heats some chemists have attempted to account for the heat evolved during combustion : state briefly the views of Craufurd and Irvine on this subject.



171. Explain the theory of combustion put forth by Berzelius and Davy.

172. How does Professor Tyndall account for the heat of combustion?

173. Describe the structure of the flame of a candle.

174. Explain the influence of elevation on the illuminating power of flames.

175. Is the presence of an incandescent solid *absolutely necessary* to the production of a luminous flame?

176. What is the common source of the halogens—chlorine, bromine and iodine?

177. How is chlorine prepared?

178. What is the composition of hydrochloric acid? How is it prepared? Give reactions. How is it identified?

179. Describe the properties of chlorine: explain how it acts as a bleaching agent.

180. What is the composition of bleaching powder? How is it made?

181. What three chlorides are *insoluble* in water? How are they distinguished?

182. Give the formula of some important chlorides.

183. How are bromine and iodine prepared?

184. Describe the natural sources of sulphur.

185. How is sulphur purified? Mention its allotropic modifications. Explain the occurrence of sulphur in volcanic districts. Describe the oxides of sulphur.

186. Mention the names of some natural sulphates and give their chemical formulæ. Describe a simple method for preparing sulphuric acid. By what tests can sulphuric acid be identified?

187. Explain the use of sulphur in making gunpowder?

188. What are the natural sources of phosphorus? How is it prepared?

189. What is the composition of the well-known manure called superphosphate? Describe the varieties of phosphoric acid. How would you distinguish them?

190. Describe the allotropic forms of phosphorus. Give the composition of the tips of matches which light only on the box.

191. How is red phosphorus prepared? What are its chief properties? What hydrogen compound of phosphorus resembles ammonia ( $\text{NH}_3$ )? How is it prepared?

192. What elements are included in the nitrogen group? What elements form the sulphur group?

193. How is ammonia gas prepared? What is the origin of its name? Describe the properties of ammonia.

194. How is nitric acid prepared? On what metals does it exert a solvent action? Which nitrates are soluble in water?

195. Exhibit the relationship of nitric acid to the several oxides of nitrogen. Which of these oxides may be used to test for free oxygen, and how?

196. Describe the mode of occurrence of silicon. What is the composition of flint, agate, and opal?

197. How is silicon prepared? Describe some of its modifications. How does hydrofluoric acid act on silicon? What is gelatinous silica?

198. What compounds of boron are commonly used? For what purpose is borax used in the art of soldering?

199. What are the natural sources of boracic acid? How is it prepared, and what are its characteristic properties?

200. In what respects does the food of plants differ from the food of animals? Give illustrations.

201. Describe roughly the composition of an average specimen of coal-gas. Which are its heat-giving and which its light-giving constituents? Name the impurities which usually occur in coal-gas. Devise methods by which they can be got rid of.

202. What are the products of the destructive distillation of wood?

203. Give a comparative statement showing the relative composition of wood and coal.

204. Explain why wood-gas has less illuminating power than coal-gas.

205. Explain the action of sulphuric acid on sugar.

206. How is marsh gas prepared? Describe its properties.

207. Describe (giving symbolic notation for the change) the mode of preparation of olefiant gas. Explain the property of this gas which effects the illuminating qualities of coal gas.

208. Describe the nature of the so-called 'Periodic Law.'

209. State Prout's hypothesis.

210. Explain the tendency of modern views in relation to elementary matter.

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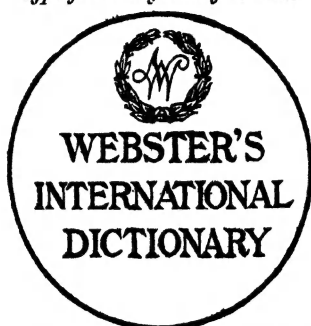
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